

## Schmeltz, Rachel

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**From:** Bronstein, Katherine [kbronstein@rti.org]  
**Sent:** Monday, May 06, 2013 1:36 PM  
**To:** Schmeltz, Rachel  
**Subject:** agenda for k call tomorrow

Hi Rachel,

Are you going to lead the discussion on the k call tomorrow? Please let me know if the agenda Keith put together works for you. The 2<sup>nd</sup> and 3<sup>rd</sup> bullets overlap a little.

- Brief introductions
- Background from Rachel on the issue(s)
- Background on what is currently in the rule and how it was developed (Jeff)
- Debbie and Susan provide summary of their research
- Open discussion of need to modify decay rate values and/or add bioreactor value and guidance.

Thanks,  
Kate

Kate Bronstein  
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## Schmeltz, Rachel

**Subject:** Decay rate values for the LF GHGRP teleconference  
**Location:** [R] MM RTP 919-316-3115 (x2-3115)  
**Start:** Tue 5/7/2013 10:00 AM  
**End:** Tue 5/7/2013 11:00 AM  
**Recurrence:** (none)  
**Meeting Status:** Accepted  
**Organizer:** Weitz, Keith A.  
**Resources:** [R] MM RTP 919-316-3115 (x2-3115)

**When:** Tuesday, May 07, 2013 10:00 AM-11:00 AM (GMT-05:00) Eastern Time (US & Canada).

**Where:** [R] MM RTP 919-316-3115 (x2-3115)

**Note:** The GMT offset above does not reflect daylight saving time adjustments.

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Call in number is 919-316-3115.

This call is to discuss comments received by EPA on the 2013 Greenhouse Gas Reporting Program (GHGRP) for municipal waste landfills (Subpart HH) regarding the lack of a proper decay rate value for "wet" landfills. We are interested in speaking with researchers on this topic via a teleconference to discuss the current decay rate value scheme used in the GHGRP and any refinements that may be appropriate to make at this time or in the future. Currently in the GHGRP for municipal landfills, the following [bulk MSW] decay rate values are used:

*ind. moderate water*  
0.02<sup>-1</sup> -- precipitation plus recirculated leachate <20 inches/year

0.038<sup>-1</sup> -- precipitation plus recirculated leachate 20-40 inches/year

0.057 yr<sup>-1</sup> -- precipitation plus recirculated leachate >40 inches/year

20%  
33%  
47%  
} Pop'ln

These and additional decay rate values by waste item(s) are included in Table HH-1 of Subpart HH of Part 98 which can be viewed here:

[http://www.ecfr.gov/cgi-bin/text-](http://www.ecfr.gov/cgi-bin/text-idx?c=ecfr&SID=7f5de87d033829571b26e8b6b8c6f63e&rgn=div9&view=text&node=40:22.0.1.1.3.34.1.10.48&idno=40)

[idx?c=ecfr&SID=7f5de87d033829571b26e8b6b8c6f63e&rgn=div9&view=text&node=40:22.0.1.1.3.34.1.10.48&idno=40](http://www.ecfr.gov/cgi-bin/text-idx?c=ecfr&SID=7f5de87d033829571b26e8b6b8c6f63e&rgn=div9&view=text&node=40:22.0.1.1.3.34.1.10.48&idno=40)

Enhanced landfills (i.e., bioreactors, wet landfills) are not a distinct/separate category in the GHGRP for landfills. They can, however, be accounted for using the upper range decay rate value for sites with precipitation and leachate recirculation greater than 40 inches per year. Different sources of k-values for enhanced sites, compared to the rule, are as follows:

**Source**

**Conditions      Recommended**

**k-value**

GHGRP Landfills with >40 inches precip/leachate recirc/year 0.057

Draft AP-42 Wet landfill 0.3

Reinhart, 2005 Landfills with liquid addition 0.11 – 0.21

Tolaymat, 2010 Bioreactors 0.11

LANDGEM Wet landfills 0.07

Kim et al, 2012 Bioreactors 0.21 – 0.47

We'd like to discuss potential changes to the GHGRP decay rate values and the potential addition of a decay rate for enhanced sites with moisture addition. Ultimately, we'd like to identify information that's available and discuss whether an amendment to Subpart HH should be undertaken to provide a different decay rate value for enhanced landfills.

Date: June 12, 2013

To: Rachel Schmeltz, EPA

From: Kate Bronstein and Jeff Coburn

Subject: Meeting Minutes for Meetings to Discuss the Decay Rate Constants (k-values)  
Used in the Greenhouse Gas Reporting Program: May 7, 2013 and May 14, 2013.

Representatives of the U.S. Environmental Protection Agency (EPA) and their contractor (RTI International) participated in two meetings with technical experts in the field of methane generation from landfills to discuss the default decay rate constants (k-values) used in the EPA's Greenhouse Gas Reporting Program (GHGRP), specifically for subpart HH (Municipal Solid Waste Landfills).

#### **Attendees**

##### Technical Experts

Dr. Debra Reinhart, University of Central Florida (5/7/13 only)

Dr. Mort Barlaz, North Carolina State University (5/14/13 only)

Jon Powell, Innovative Waste Consultants (5/14/13 only)

##### U.S. EPA Representatives

Rachel Schmeltz (5/17/13 and 5/14/13)

Susan Thorneloe (5/7/13 only)

##### RTI International (EPA contractor)

Kate Bronstein (5/17/13 and 5/14/13)

Jeff Coburn (5/17/13 and 5/14/13)

#### **Discussion Topics**

Both meetings began with a background regarding the rationale behind the k-values that are currently in the GHGRP. The GHGRP proposed three different k values for bulk waste (0.02, 0.038, and 0.057 yr<sup>-1</sup>) binned by precipitation ranges. EPA received comments at proposal that leachate recirculation should be considered and that landfills with leachate recirculation should use a higher decay rate to estimate methane generation. EPA finalized the binned approach and included "precipitation plus leachate recirculation" in defining the bin ranges to allow landfills that use leachate recirculation to use the highest k-value. The EPA received additional comments suggesting that the highest k value is too low for landfills that use leachate recirculation and should be increased.

Using precipitation as a proxy for moisture content and as a means to assign k-values was discussed. The key parameter impacting waste degradation and, consequently, methane generation is the moisture content of the waste. All were in agreement that precipitation values do not necessarily correlate with the moisture content of the waste. Landfills that use recirculation generally do so to enhance biodegradation and generally have a higher moisture content. It was agreed that moisture content of the waste was a difficult parameter to determine in the field and that it would not be practical to have landfill owners or operators attempt to measure and report the moisture content of the waste in the landfill.

The leachate collection rate per acre of landfill was also discussed as a potential surrogate for binning the k values. Leachate collection rates, as opposed to precipitation, would more closely relate to the amount of water that percolates through the landfill in a given year. Some precipitation may simply run off the landfill rather than percolate through it. It was noted that leachate collection rates are not currently required to be measured or reported, thus using leachate recirculation would add burden to entities reporting under the GHGRP. All were in agreement that although not a perfect surrogate, using precipitation and leachate recirculation rates is a reasonable method to bin the k-values.

The appropriateness of the k-values included in the GHGRP was then discussed. Commenters on the GHGRP have suggested that the EPA should use a k-value of  $0.3 \text{ yr}^{-1}$  as reported in the draft AP-42 document for "wet landfills."<sup>1</sup> The technical experts agreed that the k-value for "wet landfills" included in the draft AP-42 document was the high end of a range, and is ultimately too high to use outside of optimal landfill conditions. The  $0.3 \text{ yr}^{-1}$  value was included in the AP-42 without the qualifying criteria to justify using the high end of the study's range. The EPA representative responsible for updating AP-42 indicated that the EPA did not intend to finalize this value and the final k-value for wet landfills was more likely to be between  $0.11$  and  $0.14 \text{ yr}^{-1}$ . The technical experts also agreed that the k-value of  $0.057 \text{ yr}^{-1}$  included in the GHGRP was too low for "wet landfills" or landfills that use leachate recirculation across a majority of their landfill.

Adding a fourth bin for "wet landfills" was discussed. One option discussed was establishing a fourth bin for landfills with precipitation plus leachate recirculation rates  $>60$  inches a year. Another option was to redefine the third bin to be based only on precipitation ( $>40$  inches of precipitation per year) and add a fourth bin to be  $>40$  inches of precipitation per year, including leachate recirculation for 50 percent or more of the landfill. The technical experts suggested revised values for the third bin ranging from  $0.07$  to  $0.09 \text{ yr}^{-1}$  and suggested values for the fourth bin ranging from  $0.11$  to  $0.21 \text{ yr}^{-1}$ .

A brief discussion on how changes in the k-values could be implemented in the rule was initiated. Currently, the k-values are fixed for a given landfill and waste type. If the k-values were revised, landfills would need to revise and resubmit past reports. Additionally, a question was raised regarding how a reporter would handle changes in the use of leachate recirculation

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<sup>1</sup> United States Environmental Protection Agency, 2008. AP-42, Fifth Edition, Volume I Chapter 2: Solid Waste Disposal, Section 2.4 Municipal Solid Waste Landfills (Draft). October 2008. Available at <http://www.epa.gov/ttn/chief/ap42/ch02/draft/d02s04.pdf>.

with a fourth bin defined as ">40 inches of precipitation and practices leachate recirculation for 50 percent or more of the landfill." One suggestion included using k-values in Equation HH-1 that are a function of the disposal year. In other words, a change to the rule would need to be made to allow reporters to use different k-values over time versus selecting the most applicable k-value for the past 10 years or operating life of the landfill (whichever is shorter). EPA representatives acknowledged that changing the k-values in the GHGRP was not necessarily a trivial matter and that these issues would need to be thought through prior to amending the k-values in the GHGRP.

### Summary of Recommendations

Table 1 summarizes the k values currently in the GHGRP and recommendations for revising the default k-value for the third bin and the addition of a fourth bin.

**Table 1. Summary of Recommendations for k Values for Bulk Waste**

Current k Bin Description in the GHGRP	Suggested k Bin Description	Current Default Value	Suggested Default Value	Units
1) precipitation plus recirculated leachate < 20 inches/year	1) precipitation plus recirculated leachate < 20 inches/year	0.02	0.02	yr <sup>-1</sup>
2) precipitation plus recirculated leachate 20-40 inches/year	2) precipitation plus recirculated leachate 20-40 inches/year	0.038	0.038	yr <sup>-1</sup>
3) precipitation plus recirculated leachate > 40 inches/year	3) precipitation plus recirculated leachate >40 but ≤ 55 or 60 inches/year OR 3) precipitation >40 inches/year, but no or little leachate recirculation	0.057	0.07 to 0.09	yr <sup>-1</sup>
4) Not applicable	4) precipitation plus recirculated leachate >55 or 60 inches/year OR 4) precipitation >40 inches/year AND leachate recirculation for 50 percent or more of the landfill waste area	Not applicable	0.11 to 0.21	yr <sup>-1</sup>

## Schmeltz, Rachel

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**From:** Schmeltz, Rachel  
**Sent:** Tuesday, May 14, 2013 11:32 AM  
**To:** barlaz@ncsu.edu; Keith; Jon Powell  
**Subject:** RE: Papers to consider

Thanks so much Mort for these papers and for your time this morning.

Best,  
Rachel

-----Original Message-----

**From:** Morton Barlaz [mailto:barlaz@ncsu.edu]  
**Sent:** Tuesday, May 14, 2013 11:28 AM  
**To:** Schmeltz, Rachel; Keith; Jon Powell  
**Subject:** Papers to consider

As a follow-up to today's call, attached are 2 papers that have some gas data and estimated decay rates.

Let me know if you would like to discuss anything further and best regards.

Mort

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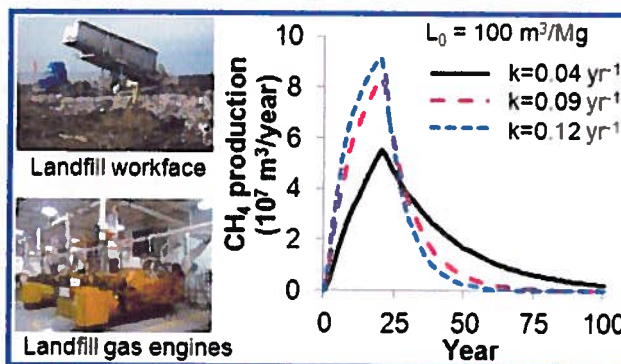
## Using Observed Data To Improve Estimated Methane Collection from Select U.S. Landfills

Xiaoming Wang,\* Ajay S. Nagpure, Joseph F. DeCarolis, and Morton A. Barlaz

Department of Civil, Construction, and Environmental Engineering, Campus Box 7908, North Carolina State University, Raleigh, North Carolina 27695-7908, United States

### Supporting Information

**ABSTRACT:** The anaerobic decomposition of solid waste in a landfill produces methane, a potent greenhouse gas, and if recovered, a valuable energy commodity. Methane generation from U.S. landfills is usually estimated using the U.S. EPA's Landfill Gas Emissions Model (LandGEM). Default values for the two key parameters within LandGEM, the first-order decay rate ( $k$ ) and the methane production potential ( $L_0$ ) are based on data collected in the 1990s. In this study, observed methane collection data from 11 U.S. landfills and estimates of gas collection efficiencies developed from site-specific gas well installation data were included in a reformulated LandGEM equation. Formal search techniques were employed to optimize  $k$  for each landfill to find the minimum sum of squared errors (SSE) between the LandGEM prediction and the observed collection data. Across nearly all landfills, the optimal  $k$  was found to be higher than the default AP-42 of  $0.04 \text{ yr}^{-1}$  and the weighted average decay for the 11 landfills was  $0.09 - 0.12 \text{ yr}^{-1}$ . The results suggest that the default  $k$  value assumed in LandGEM is likely too low, which implies that more methane is produced in the early years following waste burial when gas collection efficiencies tend to be lower.



### INTRODUCTION

An estimated 389 million tons of municipal solid waste (MSW) was generated in the U.S. in 2008, of which 69% was disposed by landfill.<sup>1</sup> Recycling and composting accounted for 24%, while the balance (7%) was burned in mass burn waste-to-energy facilities. Landfill gas (LFG) contains approximately equal volumes of methane and carbon dioxide — the major end products of biological waste decomposition in a landfill — along with some trace components.<sup>2</sup> The fate of this methane varies depending on landfill practice. Ideally, all generated methane would be captured for beneficial use. However, even at modern landfills, some methane escapes prior to installation of gas collection systems and some methane is not captured by collection systems (i.e., fugitive emissions). A fraction of the uncollected methane is oxidized in the landfill cover.<sup>3</sup> Nonetheless, landfills are estimated to account for 16.2% of anthropogenic methane emissions in the U.S.<sup>4</sup> While there is increasing interest in diverting biodegradable waste from landfills, even if all landfill disposal of biodegradable waste were discontinued in the next few years, existing landfills would remain a significant source of methane for years to come.

The U.S. EPA's LFG Emissions Model (LandGEM) is a simple equation for predicting methane production that is used at many levels (e.g., site-specific, statewide). LandGEM is a function of two model parameters:  $L_0$ , which represents the methane production potential ( $\text{m}^3 \text{Mg}^{-1}$  wet waste [ $\text{Mg}$  = metric ton]) and  $k$ , which represents the first-order decay rate

associated with waste decomposition ( $\text{yr}^{-1}$ ).<sup>5</sup> In developing the current default parameters used in LandGEM, the EPA relied on data that were collected over 15 years ago and reflect landfill management practices (e.g., waste composition, cover, gas collection efficiency) that are representative of the early 1990s.<sup>6</sup> More recently, information on waste composition has improved as landfill owners categorize waste into that containing biodegradable (e.g., residential and commercial waste, bio-solids) and inert (e.g., auto shredder waste, contaminated soil, foundry sand) fractions. Similarly, better data are available on component-specific methane yields.<sup>7–9</sup> Landfill operations have also changed as the burial of construction and demolition (C&D) waste has decreased. Finally, our understanding of LFG collection efficiency has improved.<sup>10,11</sup> These changes warrant work to update and improve current estimates of methane production and collection. The need for such improvements is highlighted in the EPA's AP-42 database, which states that "Although the recommended default  $k$  and  $L_0$  are based upon the best fit to 21 different landfills, the predicted methane emissions ranged from 38 to 492% of actual ...".<sup>6</sup> Because methane is both a potent greenhouse gas and a valuable low carbon fuel, improved predictability of landfill methane

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Table 1. General Characteristics of Landfills Selected for Study

landfill	location	annual precipitation <sup>a</sup> (cm)	annual temperature <sup>a</sup> (°C)	year opened	year closed	MSW content <sup>c</sup> (%)
S	NC	127.1	15.2	1974	open <sup>b</sup>	65
G	WI	83.3	6.6	1986	open	69
H	WI	83.3	6.6	1999	open	33
T	PA	114.3	9.6	1988	open	85
C1	NY	111.0	7.8	1958	open	76
P1	NC	127.1	15.2	1990	2004	85
M	VA	113.6	13.1	1995	open	89
Q	IL	103.2	11.3	1998	open	49
C2	MI	84.0	7.3	1989	open	49
P2	MO	111.8	12.7	2000	open	85
N	NC	127.1	15.2	1986	2008	85

<sup>a</sup>Annual precipitation and temperature values represent 20 yr averages from 1992 to 2011. The historical data were obtained from ref 19. <sup>b</sup>Landfill S was accepting waste at the time of this study, but the methane recovery data used for the analysis were obtained only from the closed area at this site due to data completeness. <sup>c</sup>The fraction of total waste comprised of MSW. The value is the average of available annual data and was assumed as 85% for Landfills P1, P2, and N where waste composition data were not available.

production is desirable. A reliable methane production model is central to any effort to improve methane emissions estimates and to ensure that energy recovery from landfills is pursued to the fullest extent. Calculations of methane production are difficult to validate; however, because the generated methane has multiple fates, including leakage to the atmosphere, oxidation in the landfill cover, and removal through collection wells.

Historically, there have been efforts to estimate LFG decay rates, as this parameter governs the rate at which gas is produced. Börjesson et al.<sup>12</sup> referenced values of 0.094, 0.05, and 0.17 yr<sup>-1</sup> for Dutch, British, and German landfills respectively based on studies done in the early 1990s. In a survey of U.S. landfills, multiple analytical methods were explored to estimate *k* and values of 0.03–0.08 yr<sup>-1</sup> were suggested for U.S. landfills including some in arid regions.<sup>13</sup> Decay rates for landfills that are operated to enhance the rate of decomposition (e.g., bioreactor landfills) have been reported to range from 0.08–0.3.<sup>14–16</sup> Amini et al.<sup>17</sup> reported decay rates of 0.04–0.13 yr<sup>-1</sup> for five Florida landfills and were the first to consider the fraction of produced gas that was collected. We build on this work by conducting a survey of 11 landfills across a broader geographical area and employ formal search techniques to find the optimal value of *k*.

The objective of this study was to develop an improved data set and model to predict methane collection from U.S. landfills. Methane collection data were used in an inverse model to estimate the best-fit *k* across a range of *L*<sub>0</sub>. LFG collection data were obtained from nine operating and two closed landfills along with schedules for waste disposal, and cover and gas collection well installation. These data were used to estimate the methane collection efficiency, which was explicitly included in LandGEM, converting it from a model that predicts methane generation to one that predicts methane collection. The revised LandGEM equation was then employed in an inverse model that minimized the sum of squared errors between calculated and observed methane collection by optimizing the decay rate (*k*) at a fixed *L*<sub>0</sub>. Additional background on LandGEM is presented in the following section, followed by information on data collection and analysis. Estimates of *L*<sub>0</sub> were derived from waste composition data and these estimates were in turn used in the optimization model to estimate *k*.

## METHODS

**Data Collection.** Landfills were selected from a pool suggested by multiple landfill owners based on data availability. General characteristics of the study landfills are summarized in Table 1. Only landfills in nonarid regions of the U.S. (>635 mm annual precipitation) were considered. The study was restricted to landfills that accept primarily MSW, which includes commercial and institutional waste, but excludes C&D waste and inert industrial waste.<sup>18</sup> Only MSW was assumed to have methane potential and the mass of nondegradable wastes was subtracted from the mass received. At most landfills, the owners provided annual data on the fraction of non-MSW waste, as shown in Table 1. However, at Landfills P1, P2, and N, the owners only suggested that the waste was mostly MSW and 85% MSW was assumed. The waste fill history for at least 10 years was required. Interestingly, despite statements that a landfill accepted primarily MSW, the annual average MSW content was 33, 49, and 49% at Landfills H, Q, and C2, respectively.

Gas data were provided as weekly or monthly point measurements and monthly averages were used for analysis. Landfills had a minimum of 5 yr of monthly data for the LFG collection rate and methane content, except landfill C2 with only ~3 yr of useable data. Finally, selected landfills were required to have historical information on the installation and operation of the gas collection and control system (GCCS). A schedule for each landfill was developed, which included the timing of waste burial in each disposal area, GCCS installation and final cover application. This information was used to estimate the gas collection efficiency as a function of the waste age and landfill area in which waste was buried.

**LandGEM Formulation.** LandGEM is widely used in practice for predicting methane generation in the U.S. and is represented by a first-order decay equation:

$$Q_n = kL_0 \sum_{i=0}^n \sum_{j=0.0}^{0.9} \frac{M_i}{10} e^{-kt_{i,j}} \quad (1)$$

where *Q*<sub>*n*</sub> is the CH<sub>4</sub> generation rate (m<sup>3</sup> yr<sup>-1</sup>) in year *n*; *k* is first-order waste decay rate (yr<sup>-1</sup>); *L*<sub>0</sub> is the CH<sub>4</sub> generation potential (m<sup>3</sup> Mg<sup>-1</sup> wet waste); *M*<sub>*i*</sub> is the waste mass placement in year *i* (Mg); *j* is an intra-annual time increment used to calculate CH<sub>4</sub> generation; and *t* is time (yr).<sup>5</sup> For this analysis,

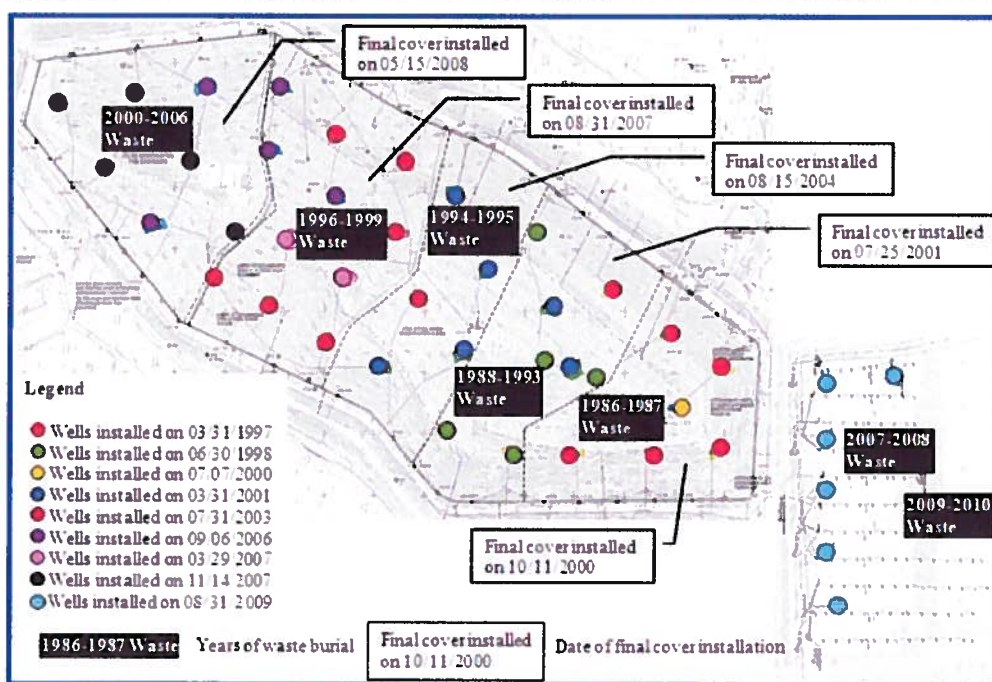


Figure 1. Location of waste disposal and schedule of final cover and GCCS installation at Landfill G. The waste buried in 2007–2010 was in an expansion adjacent to the original landfill as shown.

eq 1 was reformulated to: (1) calculate methane collection on a monthly basis, and (2) include a collection efficiency term to enable direct comparison between calculated and observed methane collection. The reformulated LandGEM equation, which calculates collected methane, is given in eq 2:

$$Q_j = \frac{kL_0}{12} \sum_{i=1}^j \alpha_{ji} M_i e^{-k\left(\frac{j-i}{12}\right)} \quad (2)$$

where  $Q_j$  is the monthly  $\text{CH}_4$  collection rate ( $\text{m}^3 \text{ month}^{-1}$ ) in month  $j$ ;  $\alpha_{ji}$  is the monthly gas collection efficiency associated with mass deposited in month  $i$  and collected in month  $j$ ; and  $M_i$  is the waste mass placed in month  $i$  (Mg). Note that the collected methane is summed over all deposition months  $i$  until a given collection month  $j$ . As a result,  $Q_j$  is recalculated for each collection month  $j$  for which observed landfill data are available. Because waste deposition might end prior to gas collection, all  $M_i$  for which  $i$  is greater than the last waste deposition month are set to zero.

LFG collection efficiencies were only estimated for the period during which gas collection data were available. The gas collection efficiency for a certain year's portion of waste at a given month was estimated by considering the cover type and the presence of gas wells. For example, for waste buried in a landfill cell with no gas wells, the collection efficiency was set to zero for each month up to the time at which the waste was under the influence of a GCCS. Conversely, for portions of waste with collection wells and geomembrane final cover, the collection efficiencies were estimated to be as high as 90%. The schedule of waste placement, GCCS and final cover installation as well as estimated collection efficiencies are presented with the results.

**Determination of Model Parameters.** As shown in eq 2,  $L_0$  and  $k$  are two key parameters for estimating the methane generation rate. Two approaches to model parametrization were used to evaluate the efficacy of the reformulated

LandGEM equation. In the first approach,  $L_0$  and  $k$  were fixed at the AP-42 default values of  $100 \text{ m}^3 \text{ Mg}^{-1}$  wet waste and  $0.04 \text{ yr}^{-1}$  respectively for landfills in regions with annual precipitation greater than  $635 \text{ mm}$ .<sup>6</sup> The mass of waste disposed included the mass of MSW but not the mass of other inert wastes that were received. The mass of biosolids received was also subtracted where possible, as biosolids would be expected to decompose before GCCS installation and thus not generate collectable methane.

In the second approach,  $L_0$  was fixed within a plausible range between 55 and  $100 \text{ m}^3 \text{ CH}_4 \text{ Mg}^{-1}$  of wet waste and  $k$  was optimized to produce the minimum sum of squared errors (SSE) between measured and calculated methane collection. In both approaches, the methane production potential  $L_0$  was fixed, because as defined,  $L_0$  is an intrinsic property of the waste and therefore a function of waste composition. Estimation of  $L_0$  as a function of waste composition is discussed in the Results.

Optimization of  $k$  for each landfill was carried out by minimizing the SSE (eq 3):

$$\text{SSE} = \sum_{j=1}^m (Q_{\text{calcd},j} - Q_{\text{meas},j})^2 \quad (3)$$

where  $j$  ranges over the total number of months during which measured  $\text{CH}_4$  collection data were available for each landfill;  $Q_{\text{calcd},j}$  is the monthly methane collection rate calculated from eq 2; and  $Q_{\text{meas},j}$  is the observed monthly methane collection rate,  $\text{m}^3 \text{ mo}^{-1}$ . To ensure consistent results, the SSE minimization was executed in both *Excel* (using Solver's Generalized Reduced Gradient method) and *MatLab* (using both the Levenberg–Marquardt algorithm and the Trust-Region-Reflective algorithm available through the *lsqcurvefit* function). In the first approach, with  $k$  and  $L_0$  fixed at the AP-42 defaults, the right-hand side of eq 3 was calculated directly without optimization.

**Table 2. Estimates of Monthly Collection Efficiency ( $\alpha_{\mu}$ ) from 2005 through 2010 for Gas Generated at Landfill G (%)<sup>a</sup>**

gas recovery period <sup>b</sup>	years of waste burial						
	1986–1995	1996–1999	2000–2004	2005–2006	2007	2008	2009–2010
01/05–09/06	90	60	0	0	0	0	0
10/06–06/07	90	75	40	0	0	0	0
07/07–11/07	90	90	40	0	0	0	0
12/07–06/08	90	90	75	75	0	0	0
07/08–08/09	90	90	90	90	0	0	0
09/09–06/10	90	90	90	90	20	0	0
07/10–12/10	90	90	90	90	75	50	0

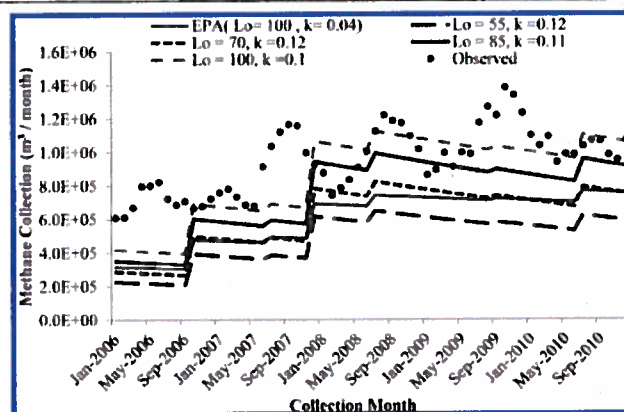
<sup>a</sup>Collection efficiency was estimated using expert judgment based on cover type, and the schedule of waste placement and GCCS installation. For example, the first row indicates that between Jan. 2005 and Sep. 2006, the LFG collection efficiencies were estimated as 90% for waste buried from 1986 through 1995; 60% for waste buried from 1996 through 1999; and zero for waste buried after 1999. <sup>b</sup>Observed methane collection data were available from Jan. 2005 through Dec. 2010, so the collection efficiencies required to calculate methane collected were only estimated for this period.

## RESULTS AND DISCUSSION

**Estimate of Monthly Collection Efficiency.** Information on the location of waste disposal within each landfill as well as the schedule of cover and GCCS installation were used to estimate LFG collection efficiency for each increment of waste disposal on a monthly basis. Figure 1 illustrates the timing of waste disposal, cover, and GCCS installation for landfill G, and Table 2 presents estimates of monthly gas collection efficiency. Similar information for each landfill is presented in Tables S1–S10 and Figures S1–S10 of the Supporting Information.

**Estimate of  $L_0$  from MSW Composition Data.** The methane production potential ( $L_0$ ) was estimated from primary data as described in this section. Previously, Staley and Barlaz<sup>8</sup> used waste discard composition data to estimate  $L_0$  as 59.1 and 63.9 m<sup>3</sup> CH<sub>4</sub> Mg<sup>-1</sup> wet refuse for national and state average waste characterization data, respectively. Here, updated methane yields for wood are used to modify the published range. Specifically, the methane yield of wood was estimated to be 11.7 m<sup>3</sup> CH<sub>4</sub> dry Mg<sup>-1</sup> based on measurements for multiple types of wood as presented in Table S11 of the Supporting Information.<sup>9</sup> Application of the updated wood methane yield resulted in a range of 58.9–71.2 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup> for the 11 states (std. dev. = 4.7) and 55.7 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup> for the national average composition (Table S12 of the Supporting Information). Given that this range is well below the AP-42 value of 100 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup>, an upper limit of  $L_0$  was determined by adjusting the food waste composition to 25%, the food waste yield to 400 m<sup>3</sup> CH<sub>4</sub> dry Mg<sup>-1</sup>, and the office paper yield to 302.6 m<sup>3</sup> CH<sub>4</sub> dry Mg<sup>-1</sup>, which is based on 100% conversion of the cellulose and hemicellulose in office paper to CH<sub>4</sub> and CO<sub>2</sub>. This results in an  $L_0$  of 82.2 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup>. For comparison, the IPCC first-order decay model results in a point estimate  $L_0$  of 89 with a range of 56–131 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup>.<sup>20</sup> While estimates of  $L_0$  based on composition exclude some non-MSW materials such as biosolids; biosolids decompose rapidly and before a GCCS is operable, and thus are unlikely to affect data sets of collected gas. Given the calculated range of  $L_0$  and the AP-42 default,  $L_0$  was varied parametrically by repeating the SSE minimization at  $L_0$  of 55, 70, 85, and 100 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup>.

**Results from Inverse Modeling.** For each of the 11 landfills, predicted methane collection (eq 2) was compared with observed methane collection. Scenarios considered include the AP-42 default ( $L_0$  = 100 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup>,  $k$  = 0.04 yr<sup>-1</sup>) and fixed values of  $L_0$  (55, 70, 85, 100 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup>) with optimized values of  $k$  based on eq 3. Figure 2 shows predicted methane collection for each  $L_0$  scenario and observed methane

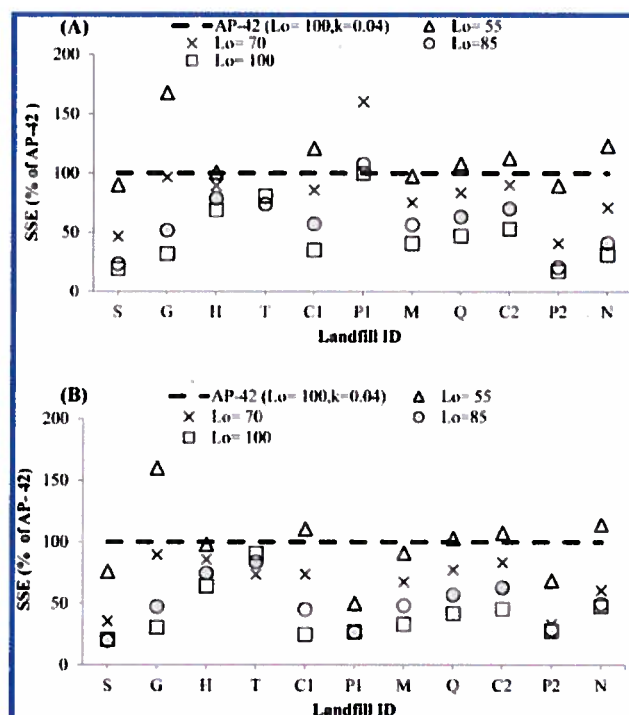


**Figure 2.** Observed methane collection from Landfill G versus estimates produced with different LandGEM parametrizations. The model was constrained to the  $L_0$  values given in the legend and the accompanying  $k$  was the value determined by minimizing the sum of squared errors.

collection data for Landfill G. Corresponding figures for the other landfills are given in Figures S11–S20 of the Supporting Information. As presented in Figure 2, the difference between the observed and predicted methane collection increases as  $L_0$  decreases, a trend that was observed for all landfills except T (Figures S11–S20 of the Supporting Information).

Part A of Figure 3 presents the minimum SSE with prescribed  $L_0$  values across all landfills at optimal, landfill-specific  $k$  values. In 3 of 11 landfills (S, M, P2), the default EPA parametrization produces the highest errors, while in the remaining 8 landfills, the largest error is produced with  $L_0$  = 55 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup>. One factor contributing to the poor match in the AP-42 default parametrization is that the low  $k$  does not enable enough methane production as, in most cases, the optimal  $k$  is well above 0.04 yr<sup>-1</sup> as discussed below. At the beginning of the collection period, the LandGEM calculations for 5 of the 11 landfills (G, H, M, C2, N) are systematically under-biased at all values of  $L_0$  compared to the observed methane collection (Figure 2, Figures S11–S20 of the Supporting Information). As a result, predicted methane is low at  $L_0$  of 55 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup>, and this contributes to a high SSE. Higher  $L_0$  values push the SSE to lower values by increasing methane production to overcome the low bias. An  $L_0$  of 100 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup> resulted in the minimum SSE at each landfill except for T, where  $L_0$  of 85 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup> was slightly better.





**Figure 3.** Sum of squared errors (SSE) observed at each landfill under different parametrizations, normalized to the error associated with the AP-42 parametrization. Part A (top) does not include a lag time, while part B (bottom) includes a 6 month lag time. The parametrizations with low  $L_0$  values result in higher error, whereas those with higher  $L_0$  values result in lower error. The SSE for Landfills T and P1 at  $L_0 = 55 \text{ m}^3 \text{ CH}_4 \text{ wet Mg}^{-1}$  (part A) are a factor of 4.4 and 5.2 higher than the AP-42 value and are not shown. The SSE for Landfill T at  $L_0 = 55 \text{ m}^3 \text{ CH}_4 \text{ wet Mg}^{-1}$  (part B) is a factor of 3.4 higher than the AP-42 value and is not shown.

The optimal  $k$  associated with each landfill and  $L_0$  parametrization was  $0.04 \text{ yr}^{-1}$  at 2 landfills and  $0.09\text{--}0.17 \text{ yr}^{-1}$  at the other nine (Table 3). The derived values of  $k$  are uncertain given the absence of precise knowledge of  $L_0$  and the need to estimate  $\alpha_i$ . Despite the uncertainty, with the exception of Landfills T and P2, the optimal  $k$  did not vary by more than 25% between  $L_0$  of 85 and  $100 \text{ m}^3 \text{ CH}_4 \text{ wet Mg}^{-1}$ , and only exhibited a sharp increase at  $L_0$  of  $70 \text{ m}^3 \text{ wet Mg}^{-1}$  for Landfill T. Given that the methane production data do not reflect the contribution of methane from the most rapidly degradable components of MSW (e.g., food waste, grass, leaves), the estimated  $k$  could be biased low.<sup>21</sup> This potential low bias is interesting as 9 of the 11 landfills have a  $k$  that is higher than the AP-42 default and 7 are higher than the IPCC range of  $0.08\text{--}0.1 \text{ yr}^{-1}$  at  $L_0 = 100 \text{ m}^3 \text{ CH}_4 \text{ wet Mg}^{-1}$ .<sup>20</sup>

To explore the significance of the low bias, the optimal  $k$  was plotted against the average waste age for each landfill, where the average waste age was calculated from the mass of MSW disposed each year. The absence of a trend (Figure S21 of the Supporting Information) suggests that the low bias did not have a noticeable influence on the results. While Landfills T and P1 had the lowest  $k$  and waste ages at the upper end of the range (7.7 and 8.1 yr), the oldest average waste age of 11.6 yr corresponded to the highest  $k$ . Landfill P1 was closed in October 2004, before the initial data were collected for this study, while Landfill T is active.

**Table 3.**  $\text{CH}_4$  Generation Potential ( $L_0$ ) and Corresponding Optimized First-Order Waste Decay Rate ( $k$ ) for Studied Landfills<sup>a</sup>

landfill	leachate recirculation <sup>b</sup>	biosolids acceptance <sup>b,c</sup>	$L_0 = 55$	$L_0 = 70$	$L_0 = 85$	$L_0 = 100^d$
S	Y	Y	0.17	0.17	0.16	0.12 (0.08–0.16)
G	Y	Y	0.12	0.12	0.11	0.10 (0.07–0.11)
H	Y	Y	0.15	0.15	0.15	0.15 <sup>e</sup>
T	Y	Y	0.12	0.12	0.06	0.04 (0.04–0.06)
C1	N	Y	0.17	0.17	0.17	0.17 (0.17–0.18)
P1	N	<sup>e</sup>	0.10	0.08	0.05	0.04 (0.03–0.05)
M	Y	<sup>e</sup>	0.17	0.17	0.17	0.17 <sup>e</sup>
Q	N	Y	0.14	0.14	0.14	0.13 (0.12–0.14)
C2	N	Y	0.15	0.15	0.15	0.15 <sup>e</sup>
P2	N	Y	0.17	0.16	0.14	0.09 (0.08–0.13)
N	N	<sup>e</sup>	0.16	0.15	0.14	0.11 (0.08–0.14)

<sup>a</sup>Units for  $L_0$  and  $k$  are  $\text{m}^3 \text{ CH}_4 \text{ wet Mg}^{-1}$  and  $\text{yr}^{-1}$ , respectively. <sup>b</sup>Y/N = yes/no. <sup>c</sup>N.A. = no biosolids information available. <sup>d</sup>The values in parentheses represent the range of  $k$  when the fraction of MSW in the buried waste was increased and decreased by 10%. The lower end of the range represents the higher MSW fraction. <sup>e</sup>No change to two significant figures.

As described above,  $L_0$  is an intrinsic property of the waste and should not be part of an optimization to determine a best fit. When both  $k$  and  $L_0$  are co-optimized without bounds, the resultant  $L_0$  is  $1816 \text{ m}^3 \text{ CH}_4 \text{ wet Mg}^{-1}$  for Landfill G and ranged from 73 to  $7721 \text{ m}^3 \text{ CH}_4 \text{ wet Mg}^{-1}$  for the other landfills. The optimal  $L_0$  was greater than  $100 \text{ m}^3 \text{ CH}_4 \text{ wet Mg}^{-1}$  in 8 of the 11 landfills. However, the composition-based estimates of  $L_0$  presented above suggest that  $L_0$  values close to or above  $100 \text{ m}^3 \text{ CH}_4 \text{ wet Mg}^{-1}$  are artificially high. This suggests that  $L_0$ , as used in eqs 2 and 3, includes the effect of unmodeled parameters which influences the results. Examples of unmodeled parameters include lag time, precipitation, and temperature and are discussed further below.

**Sources of Uncertainty in the LandGEM Parametrization.** The characterization of methane collection with a simple first-order decay equation multiplied by several scalar parameters is clearly insufficient to predict the observed monthly variability in collected methane. The discrepancy between calculated and observed methane collection, as shown in Figures 2 to 3, may be due to several factors including landfill operation, presence of biosolids, precipitation, temperature, lag time, and period of data observation.

Despite assurances from operators that the landfills visited were not operated as bioreactors, 5 of the 11 landfills recirculated leachate on some waste at some time (Table 3). While the two highest decay rates are associated with leachate recirculation (Landfills M and H), the lowest decay rate is also associated with leachate recirculation (Landfill T), and Landfills C1 and C2 have the same values as Landfills M and H but did not recirculate leachate. Thus, there is no relationship between the reported recirculation and the decay rate. This is not entirely surprising as an earlier study of bioreactor landfills showed that in many cases, leachate was only recirculated to a small section of the landfill and thus might not impact gas

generation over the entire site.<sup>15</sup> As the operators did not consider any of the landfills to be bioreactors, the extent of leachate recirculation was likely low.

The nutrient value of biosolids could stimulate methane generation even if the methane generated from the biosolids was not captured. However, 9 of the 11 landfills accepted biosolids, including landfills with the highest and lowest reported decay rates.

Higher temperature and precipitation can result in higher methane generation; however, mean annual temperature for the landfills varied over a relatively narrow range (7–15 °C) and there was no relationship between this metric and the decay rate at  $L_0$  of 100 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup> (part A of Figure 4). Similarly, there was no relationship in annual precipitation across the landfills (part B of Figure 4).

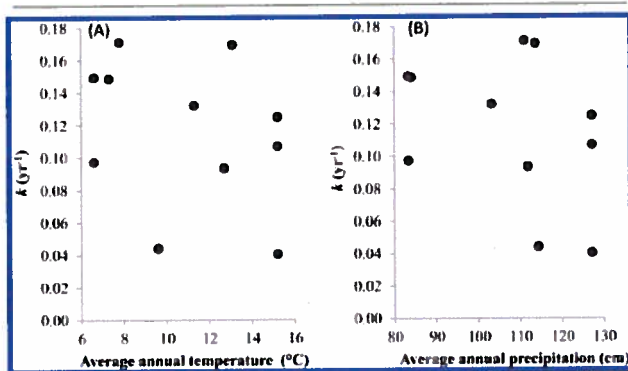


Figure 4. Optimal  $k$  values at  $L_0 = 100$  m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup> versus temperature (panel A) and precipitation (panel B) for each of the 11 landfills studied. No correlation is observed.

Although data were provided on the fraction of the total waste comprised of MSW at 8 of 11 landfills (Table 1), this fraction had to be assumed for three landfills and undoubtedly includes some variability at the other landfills. To explore the sensitivity of this assumption, decay rates were recalculated at each  $L_0$  after increasing and decreasing the assumed fraction of MSW by 10% (i.e., if the point value was 85% MSW, then  $k$  was calculated at 75 and 95% MSW). The results are given in Table 3 at  $L_0$  of 100 m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup>. The impact of this assumption varied by landfill and the ranges provided in Table 3 provide one illustration of the uncertainty in  $k$ .

LandGEM assumes that methane generation begins immediately following waste deposition; however, some lag between waste deposition and methane generation is likely, albeit hard to quantify. To test the effect of delayed methane emissions, a 6 month lag time between waste deposition and methane generation was introduced (part B of Figure 3). While the lag time effectively increases the estimate of methane generation, the small relative magnitude of the 6 month lag time compared to the multiyear collection period for each landfill results in a negligible improvement in fit between calculated and observed data except for Landfill P1.

Finally, some of the observed bias in the results may be due to the minimization of SSE over a narrow temporal window relative to the total period of methane generation for a landfill. Since the observation period varied across the 11 landfills from a minimum of 35 months (Landfill C2) to a maximum of 108 months (Landfill M), the root mean squared error (RMSE) was plotted versus observation period. RMSE is plotted instead of SSE, as the former accounts for the number of observations,

whereas the latter does not. Despite a factor of 3 variation in the observed collection period across the observed landfills, no correlation between the RMSE and observed collection period is evident (Figure S22 of the Supporting Information).

**Policy Implications.** Analyses were conducted to develop an explanatory model to predict  $k$  as a function of lag time, waste age, precipitation, and temperature. Because no clear relationship could be established and this study included less than 1% of the U.S. landfill population, we are hesitant to provide a definitive recommendation. Nonetheless, the optimized  $k$  values provide a significantly better match to the observed data than the default EPA AP-42 parametrization across the 11 landfills. A mass weighted average  $k$  of 0.09 yr<sup>-1</sup> was calculated from the cumulative mass of biodegradable waste in place (Table S13 of the Supporting Information). Landfill T accounted for 42.6% of the mass of all 11 landfills and Landfill T had the lowest decay rate. When Landfill T is excluded, the weighted average  $k$  is 0.12 yr<sup>-1</sup>. In the absence of improved data, we recommend a default  $k$  of 0.09–0.12 yr<sup>-1</sup>. Dropping the strict definition of  $L_0$  as the methane production potential, we recommend  $L_0 = 100$  m<sup>3</sup> Mg<sup>-1</sup> wet waste, which provides the best fit to observational data in 10 out of 11 landfills.

Given the simplicity of the LandGEM formulation, it is not surprising that there is considerable variability in the relationship between LandGEM and actual methane collection data. Landfills are heterogeneous ecosystems in which the waste composition, temperature, and moisture content vary both spatially and temporally. Thus, the  $k$  applicable to the waste mass also varies spatially and temporally. While varying  $k$  and  $L_0$  spatially and temporally might be mechanistically correct, there is a trade-off between a simple model with a few parameters and a complex model with more parameters but greater difficulty in deriving the appropriate parametrization. Despite all of the uncertainty and confounding variables, the analysis conducted here suggests that the AP-42 default decay rate is too low. This is significant because a higher decay rate will result in predictions of more methane generation in the early years after waste burial when gas collection efficiencies tend to be lower. Thus higher decay rates will result in higher estimates of uncollected methane in greenhouse gas inventories.<sup>4</sup> This research also suggests that it is misleading to refer to  $L_0$  as the methane production potential because the value of  $L_0$  in LandGEM includes unmodeled parameters that influence methane generation.

Further work is required to identify the controlling unmodeled parameters, explore reformulations of LandGEM that might include a slow and rapidly decomposing waste fraction, quantify uncertainty, and expand observational data sets.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Schedule of waste disposal, cover and GCCS installation, estimates of monthly collection efficiency ( $\alpha_i$ ), predicted and observed methane collection, decay rates versus average waste age, and RMSE versus observation period for all landfills; estimates of methane yield for wood waste and bulk MSW; and derivation of the weighted average decay rate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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## ■ REFERENCES

- (1) van Haaren, R.; Themelis, N.; Goldstein, N. The State of Garbage in America. *Biocycle* **2010**, *51*, 16–23.
- (2) Barlaz, M. A.; Ham, R. K.; Schaefer, D. M. Methane Production from Municipal Refuse - a Review of Enhancement Techniques and Microbial Dynamics. *Crit. Rev. Environ. Control* **1990**, *19*, 557–584.
- (3) Chanton, J. P.; Powelson, D. K.; Green, R. B. Methane Oxidation in Landfill Cover Soils, is a 10% Default Value Reasonable? *J. Environ. Qual.* **2009**, *38*, 654–663.
- (4) *Inventory of U.S. Greenhouse Gases Emissions and Sinks 1990–2010*; 430-R-12–001; U.S. Environmental Protection Agency: Washington, D.C., 2012; <http://www.epa.gov/climatechange/Downloads/ghgemissions/US-GHG-Inventory-2012-Main-Text.pdf>.
- (5) *Landfill Gas Emissions Model (LandGEM) Version 3.02 User's Guide*; U.S. Environmental Protection Agency: Washington, D.C., 2005; <http://www.epa.gov/ttn/catcl/dir1/landgem-v302-guide.pdf>.
- (6) *Compilation of Air Pollutant Emission Factors, AP-42, Vol. 1: Stationary Point and Area Sources, 5th ed., Supplement E, Chapter 2.4: Municipal Solid Waste Landfills*; U.S. Environmental Protection Agency: Washington, D.C., 1998.
- (7) Eleazer, W. E.; Odle, W. S.; Wang, Y. S.; Barlaz, M. A. Biodegradability of Municipal Solid Waste Components in Laboratory-Scale Landfills. *Environ. Sci. Technol.* **1997**, *31*, 911–917.
- (8) Staley, B. F.; Barlaz, M. A. Composition of Municipal Solid Waste in the United States and Implications for Carbon Sequestration and Methane Yield. *J. Environ. Eng.* **2009**, *135*, 901–909.
- (9) Wang, X.; Padgett, J. M.; De, I. C.; Barlaz, M. A. Wood Biodegradation in Laboratory-Scale Landfills. *Environ. Sci. Technol.* **2011**, *45*, 6864–6871.
- (10) Spokas, K.; Bogner, J.; Chanton, J. P.; Morcet, M.; Aran, C.; Graff, C.; Golvan, Y. M.; Hebe, I. Methane Mass Balance at Three Landfill Sites: What Is the Efficiency of Capture by Gas Collection Systems? *Waste Manage* **2006**, *26*, 516–525.
- (11) Barlaz, M. A.; Chanton, J. P.; Green, R. B. Controls on Landfill Gas Collection Efficiency: Instantaneous and Lifetime Performance. *J. Air Waste Manage. Assoc.* **2009**, *59*, 1399–1404.
- (12) Börjesson, G.; Samuelsson, J.; Chanton, J.; Adolfsson, R.; Galle, B. O.; Svesson, B. H. A National Landfill Methane Budget for Sweden Based on Field Measurements, and an Evaluation of IPCC Models. *Tellus: Series B* **2009**, *61*, 424–435.
- (13) *Comparison of Models for Predicting Landfill Methane Recovery*; GR-LG 0075; The Solid Waste Association of North America (SWANA): Silver Spring, MD, 1998.
- (14) Faour, A. A.; Reinhart, D. R.; You, H. First-Order Kinetic Gas Generation Model Parameters for Wet Landfills. *Waste Manage* **2007**, *27*, 946–953.
- (15) Barlaz, M. A.; Bareither, C. A.; Hossain, A.; Saquing, J.; Mezzari, I.; Benson, C. H.; Tolaymat, T. M.; Yazdani, R. Performance of North American Bioreactor Landfills. II: Chemical and Biological Characteristics. *J. Environ. Eng. -ASCE* **2010**, *136*, 839–853.
- (16) Tolaymat, T. M.; Green, R. B.; Hater, G. R.; Barlaz, M. A.; Black, P.; Bronson, D.; Powell, J. Evaluation of Landfill Gas Decay Constant for Municipal Solid Waste Landfills Operated as Bioreactors. *J. Air Waste Manage. Assoc.* **2010**, *60*, 91–97.
- (17) Amini, H. R.; Reinhart, D. R.; Mackie, K. R. Determination of First-Order Landfill Gas Modeling Parameters and Uncertainties. *Waste Manage* **2012**, *32*, 305–316.
- (18) *Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2010*; 530-F-11–005; U.S. Environmental Protection Agency: Washington, D.C., 2011; [http://www.epa.gov/osw/nonhaz/municipal/pubs/msw\\_2010\\_rev\\_factsheet.pdf](http://www.epa.gov/osw/nonhaz/municipal/pubs/msw_2010_rev_factsheet.pdf).
- (19) U.S. National Oceanic and Atmospheric Administration, National Climatic Data Center website; <http://www.ncdc.noaa.gov/temp-and-precip/time-series/index.php>.
- (20) *2006 IPCC Guidelines for National Greenhouse Gas Inventories: Vol. 5 (Chapter 3); Intergovernmental Panel on Climate Change (IPCC): Geneva, Switzerland, 2006*; [http://www.ipcc-nggip.iges.or.jp/public/gp/bgp/5\\_1\\_CH4\\_Solid\\_Waste.pdf](http://www.ipcc-nggip.iges.or.jp/public/gp/bgp/5_1_CH4_Solid_Waste.pdf).
- (21) De la Cruz, F. B.; Barlaz, M. A. Estimation of Waste Component-Specific Landfill Decay Rates Using Laboratory-Scale Decomposition Data. *Environ. Sci. Technol.* **2010**, *44*, 4722–4728.

# Using Observed Data to Improve Estimated Methane Collection from Select U.S. Landfills

## Supporting Information (SI)

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32 Pages; 13 Tables, 22 Figures

Figures S1 to S10 present the location of waste disposal and the schedule of final cover and GCCS installation at case-study landfills except for G. Figures S11 to S20 present predicted methane collection for each  $L_0$  scenario and observed methane collection data for case-study landfills except for G. The optimal decay rate as a function of average waste age is presented in Figure S21. The root mean squared error (RMSE) versus observation period for case-study landfills is illustrated in Figure S22.

Tables S1 to S10 present estimates of monthly collection efficiency ( $\alpha_{ji}$ ) for gas generated at case-study landfills except for G. Estimates of methane yield for wood waste and bulk MSW are presented in Tables S11 and S12, respectively. Table S13 presents the weighted average first order waste decay rate ( $k$ ) across all landfills.



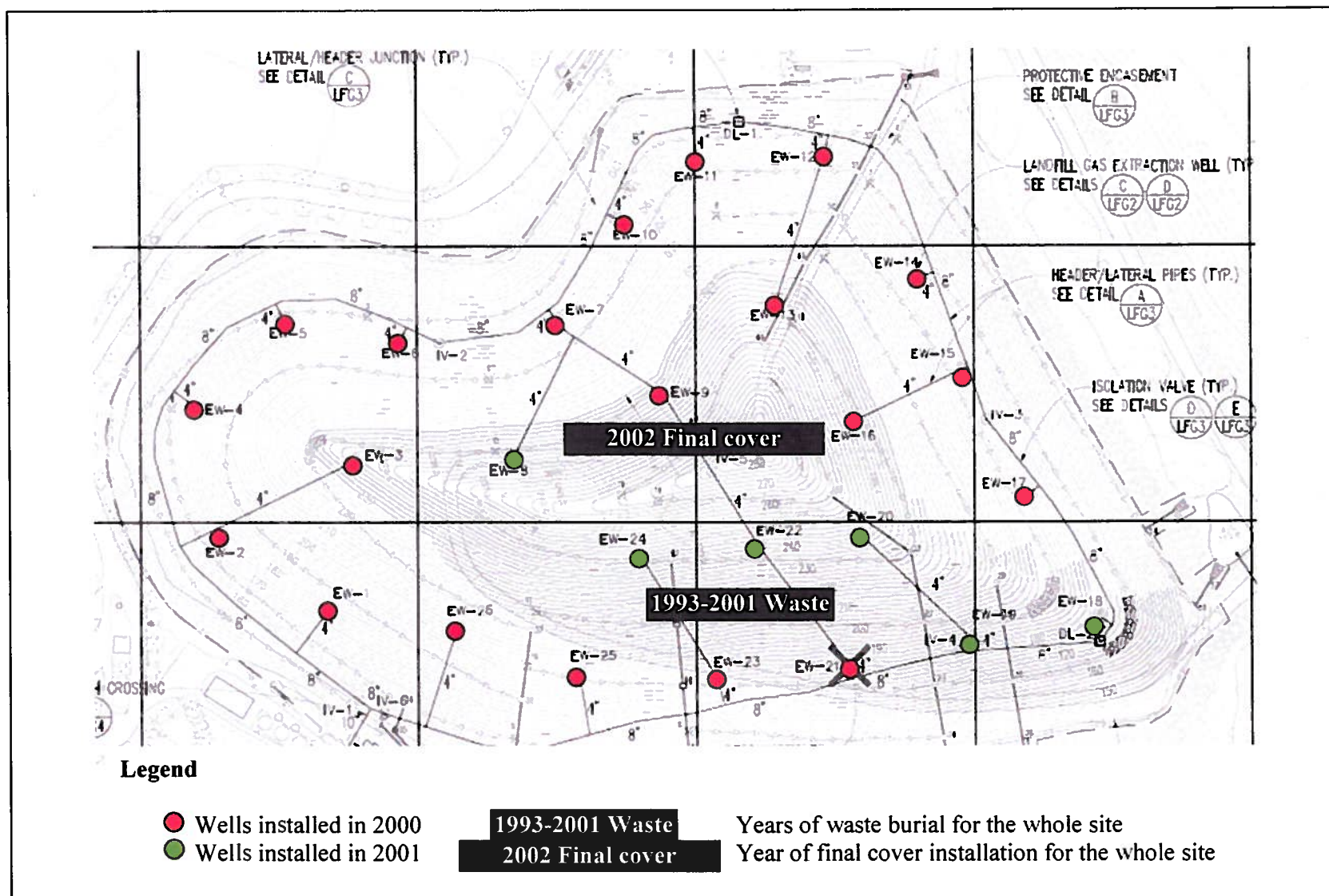


Figure S1. Location of waste disposal and schedule of final cover and GCCS installation at Landfill S.

Table S1. Estimates of Monthly Collection Efficiency ( $\alpha_i$ ) from 2003 through 2007 for Gas Generated at Landfill S (%)<sup>a</sup>

Gas recovery period	Years of waste burial 1993-2001
01/03 – 12/03	90 <sup>b</sup>
01/04 – 12/04	90 <sup>b</sup>
01/05 – 12/05	90 <sup>b</sup>
01/06 – 12/06	90 <sup>b</sup>
01/07 – 12/07	90 <sup>b</sup>

- a. Collection efficiency was estimated using expert judgment based on cover type, and the schedule of waste placement and GCCS installation. For example, the first row indicates that between Jan. 2003 and Dec. 2003, the LFG collection efficiencies were estimated as 90% for waste buried from 1993 through 2001.
- b. The gas collection wells and geomembrane final cover had been constructed by the end of 2002, so 90% collection efficiency was assumed for the gas generated from 2003 through 2007.

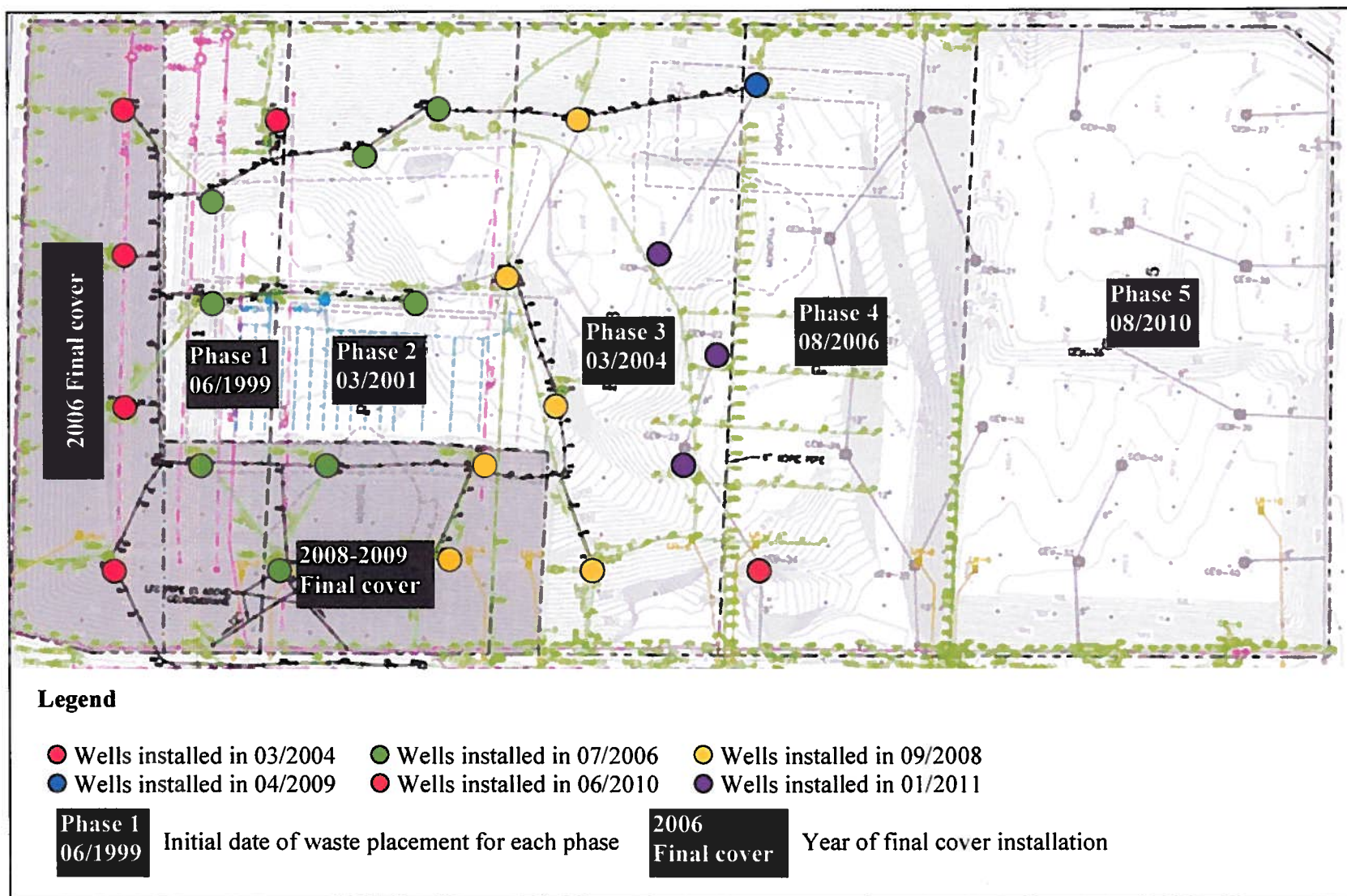


Figure S2. Location of waste disposal and schedule of final cover and GCCS installation at Landfill H.

Table S2. Estimates of Monthly Collection Efficiency ( $\alpha_{ij}$ ) from 2006 through 2010 for Gas Generated at Landfill H (%)<sup>a</sup>

Gas recovery period	Years of waste burial											
	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
01/06 – 07/06	60	60	0	0	0	0	0	0	0	0	0	0
08/06 – 06/08	90	90	40	40	40	0	0	0	0	0	0	0
07/08 – 09/08	90	90	90	75	75	0	0	0	0	0	0	0
10/08 – 04/09	90	90	90	75	75	20	20	0	0	0	0	0
05/09 – 06/09	90	90	90	75	75	20	20	10	0	0	0	0
07/09 – 12/10	90	90	90	85	85	20	20	10	0	0	0	0

- a. Collection efficiency was estimated using expert judgment based on cover type, and the schedule of waste placement and GCCS installation. For example, the first row indicates that between Jan. 2006 and July 2006, the LFG collection efficiencies were estimated as 60% for waste buried from 1999 through 2000, and zero for waste buried after 2000. The installation of final cover occurred in multiple years as shown in Figure S2. The effective date for cover installation was assumed to be July of the installation year, as the explicit dates of cover installations were not available.



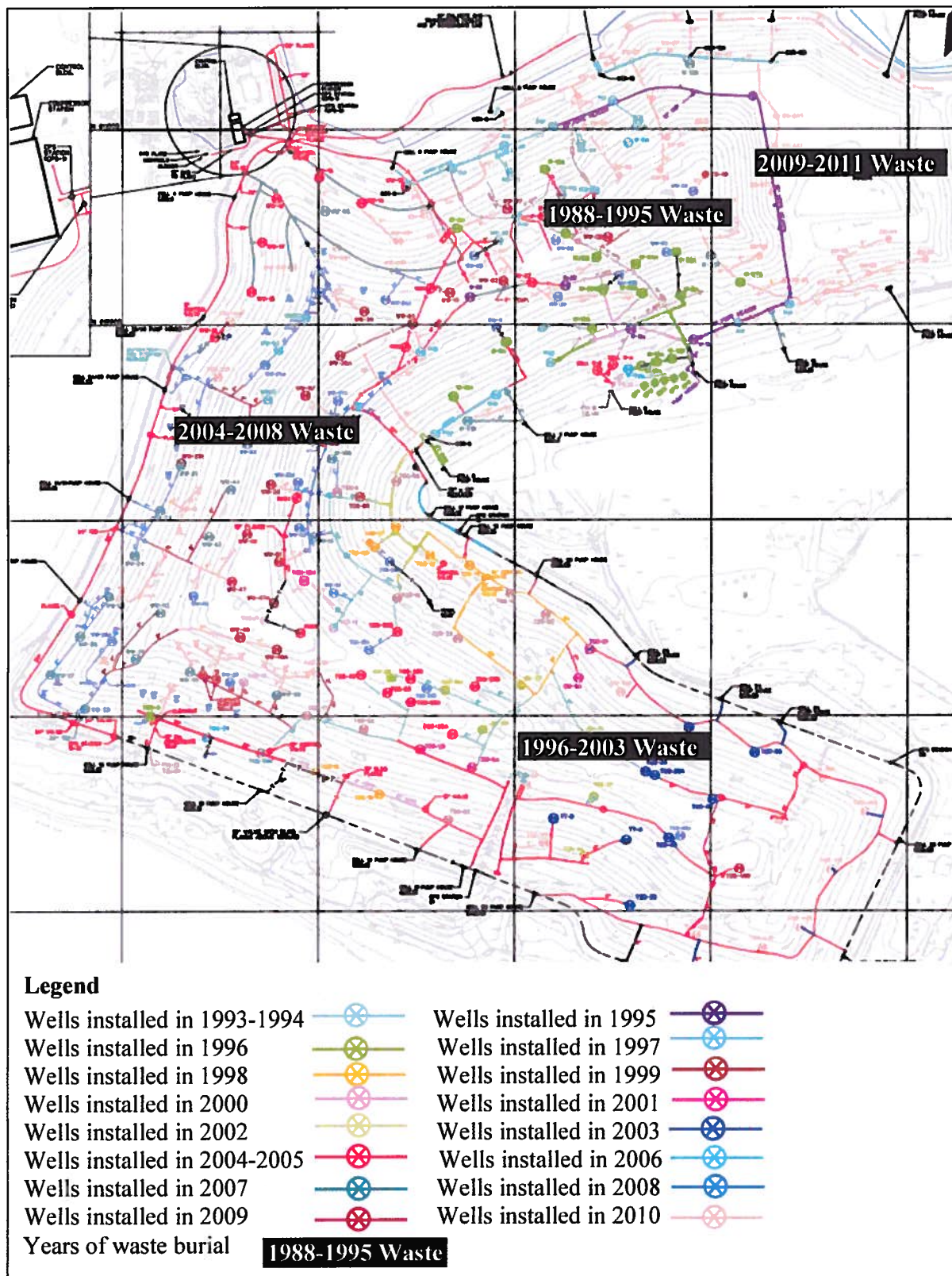


Figure S3. Location of waste disposal and schedule of final cover and GCCS installation at Landfill T.

Table S3. Estimates of Monthly Collection Efficiency ( $\alpha_{ji}$ ) from 2006 through 2011 for Gas Generated at Landfill T (%)<sup>a</sup>

Gas recovery period	Years of waste burial								
	1988-2003	2004	2005	2006	2007	2008	2009	2010	2011
01/06 – 06/06	90	0	0	0	0	0	0	0	0
07/06 – 06/07	90	60	0	0	0	0	0	0	0
07/07 – 06/08	90	75	60	0	0	0	0	0	0
07/08 – 06/09	90	75	75	60	0	0	0	0	0
07/09 – 06/10	90	75	75	75	60	0	0	0	0
07/10 – 06/11	90	75	75	75	75	60	0	0	0
07/11 – 12/11	90	75	75	75	75	75	60	0	0

- a. Collection efficiency was estimated using expert judgment based on cover type, and the schedule of waste placement and GCCS installation. This facility was aggressive with GCCS installation, which is due to its proximity to populated areas and the importance of odor control. By Jan 2006, the wastes accepted from 1998 through 2003 had been capped under a geomembrane final cover. GCCS installation events occurred in multiple years as shown in Figure S3. The effective date for gas collection wells was assumed to be July of the well installation year, as the explicit dates of well installations were not available.



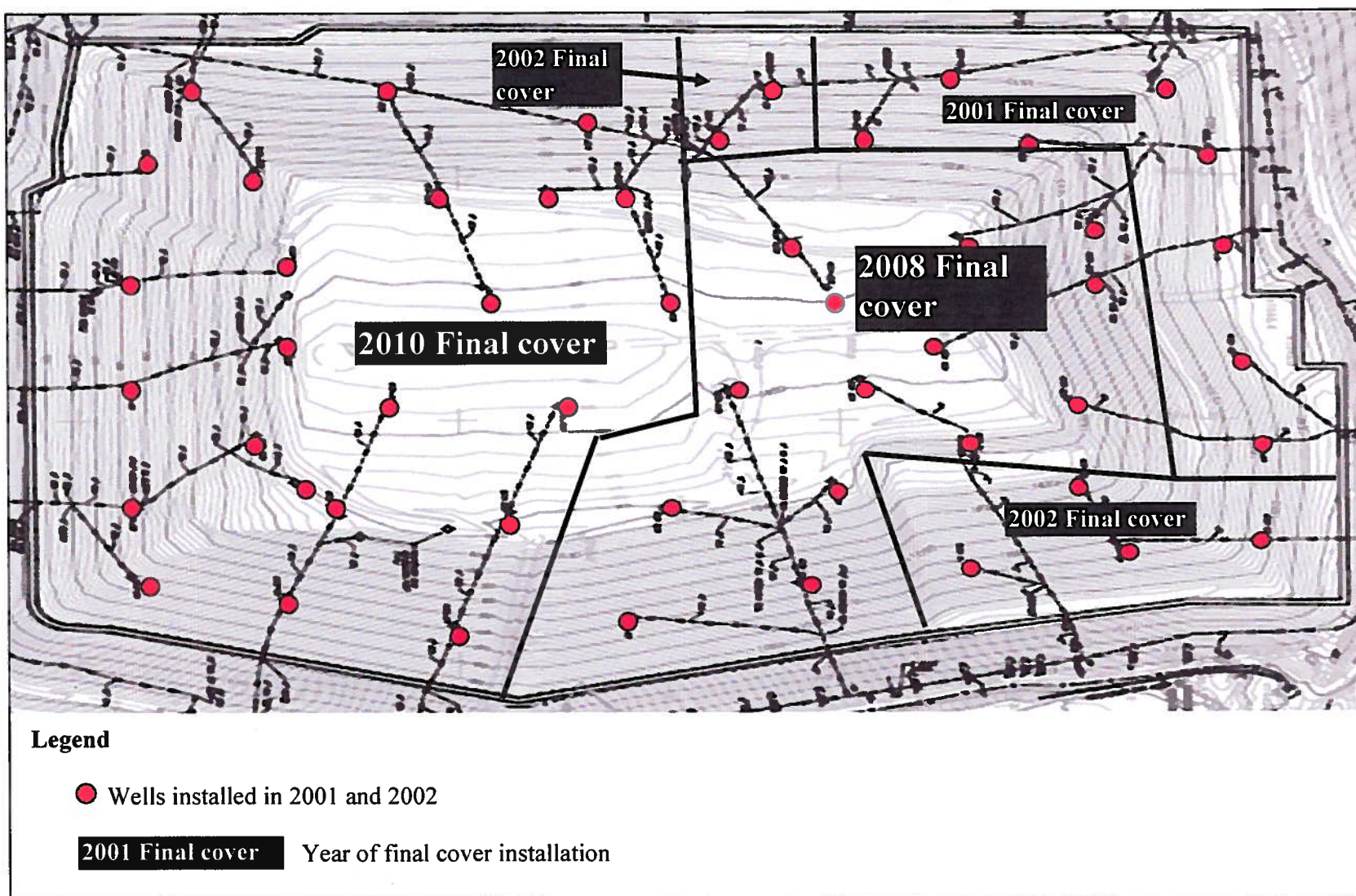


Figure S4. Location of waste disposal and schedule of final cover and GCCS installation at Landfill C1.

Table S4. Estimates of Monthly Collection Efficiency ( $\alpha_{ji}$ ) from 2003 through 2008 for Gas Generated at Landfill C1 (%)<sup>a</sup>

Gas recovery period	Years of waste burial							
	1958-2000	2001	2002	2003	2004	2005	2006	2007
01/03 – 12/03	75	50	0	0	0	0	0	0
01/04 – 12/04	75	75	50	0	0	0	0	0
01/05 – 12/05	75	75	75	50	0	0	0	0
01/06 – 12/06	75	75	75	75	50	0	0	0
01/07 – 12/07	75	75	75	75	75	50	0	0
01/08 – 12/08	85	75	75	75	75	75	50	0

- a. Collection efficiency was estimated using expert judgment based on cover type, and the schedule of waste placement and GCCS installation. In 2003 through 2007, only a small fraction of the waste mass accepted between 1958 and 2000 was capped under the geomembrane final cover. In 2008, approximately half of the waste disposal area was capped under the final cover, so the collection efficiency for waste mass accepted from 1958 through 2000 was assumed to increase from 75 to 85%.



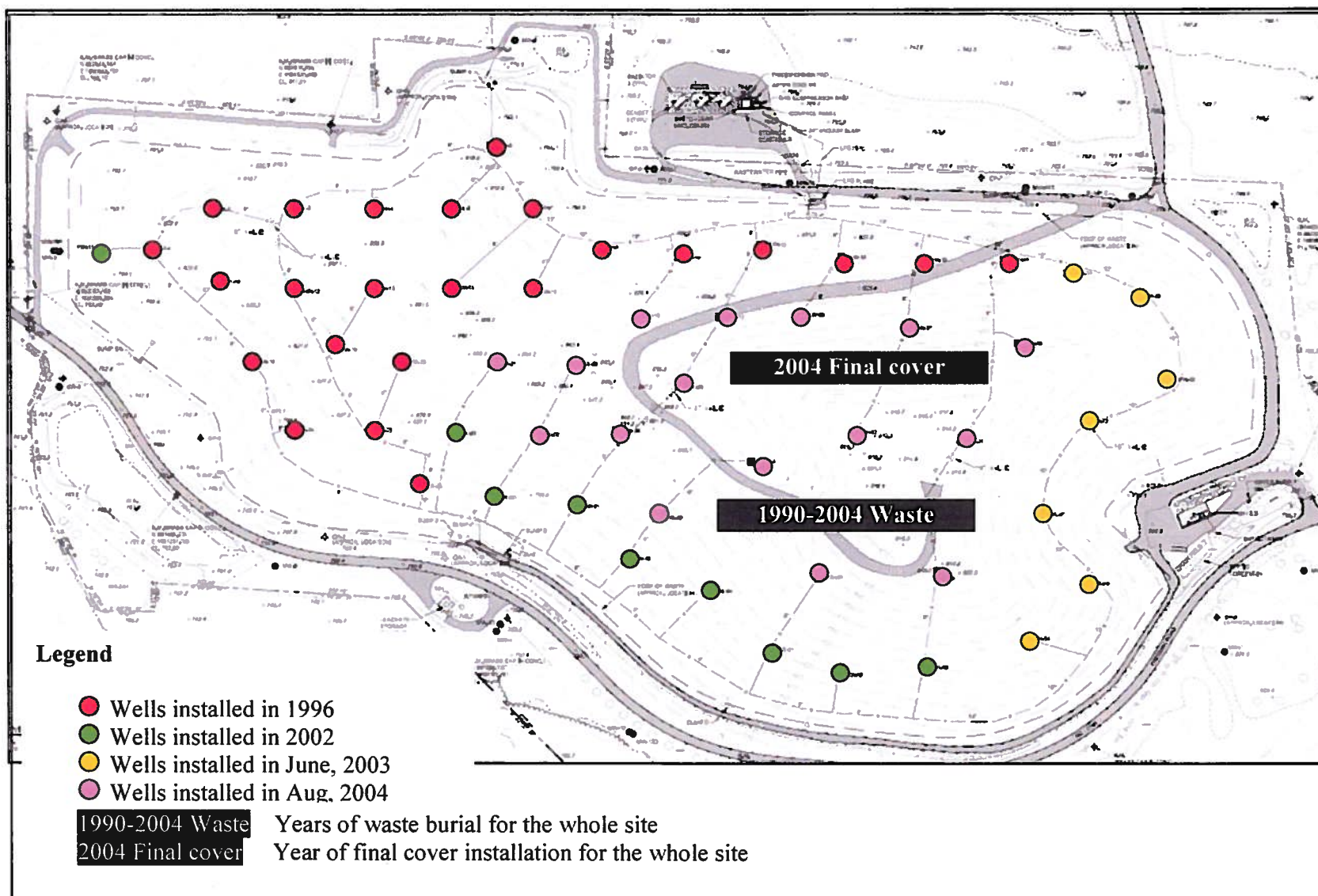


Figure S5. Location of waste disposal and schedule of final cover and GCCS installation at Landfill P1.

Table S5. Estimates of Monthly Collection Efficiency ( $\alpha_i$ ) from 2005 through 2011 for Gas Generated at Landfill P1(%)<sup>a</sup>

Gas recovery period	Years of waste burial 1990-2004
01/05 – 12/05	90
01/06 – 12/06	90
01/07 – 12/07	90
01/08 – 12/08	90
01/09 – 12/09	90
01/10 – 12/10	90
01/11 – 12/11	90

- a. Collection efficiency was estimated using expert judgment based on cover type, and the schedule of waste placement and GCCS installation. The gas collection wells and geomembrane final cover had been constructed by the end of 2004, so 90% of collection efficiency was assumed for the gas generated from 2005 through 2011.

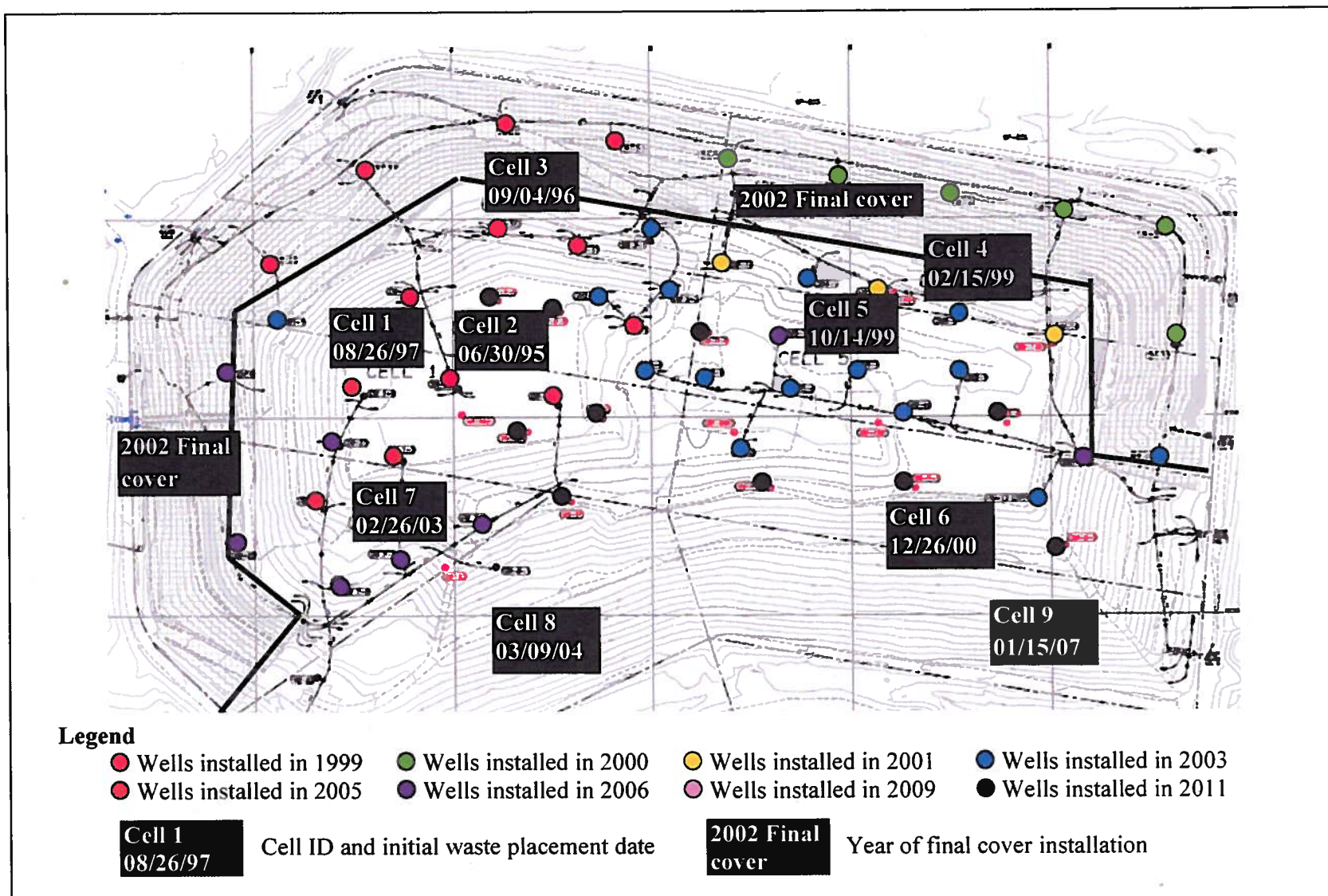


Figure S6. Location of waste disposal and schedule of final cover and GCCS installation at Landfill M.

Table S6. Estimates of Monthly Collection Efficiency ( $\alpha_{ji}$ ) from 2000 through 2010 for Gas Generated at Landfill M (%)<sup>a</sup>

Gas recovery period	Years of waste burial											
	1995-1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007-2009	2010
01/00 – 06/01	70	30	0	0	0	0	0	0	0	0	0	0
07/01 – 06/02	70	40	40	0	0	0	0	0	0	0	0	0
07/02 – 06/03	85	50	40	40	0	0	0	0	0	0	0	0
07/03 – 06/04	85	50	75	75	50	0	0	0	0	0	0	0
07/04 – 06/05	85	50	85	75	50	40	0	0	0	0	0	0
07/05 – 06/06	85	75	85	75	50	40	40	0	0	0	0	0
07/06 – 06/09	85	85	85	75	50	40	50	10	0	0	0	0
07/09 – 12/10	85	85	85	75	50	40	70	20	10	10	10	0

- a. Collection efficiency was estimated using expert judgment based on cover type, and the schedule of waste placement and GCCS installation. For gas generated from waste mass accepted after 1997, low collection efficiencies were assumed due to the low density of well coverage. Well installation events occurred in multiple years as shown in Figure S6. Gas collection wells were assumed to be effective in July of the well installation year, as the explicit dates of well installations were not available.



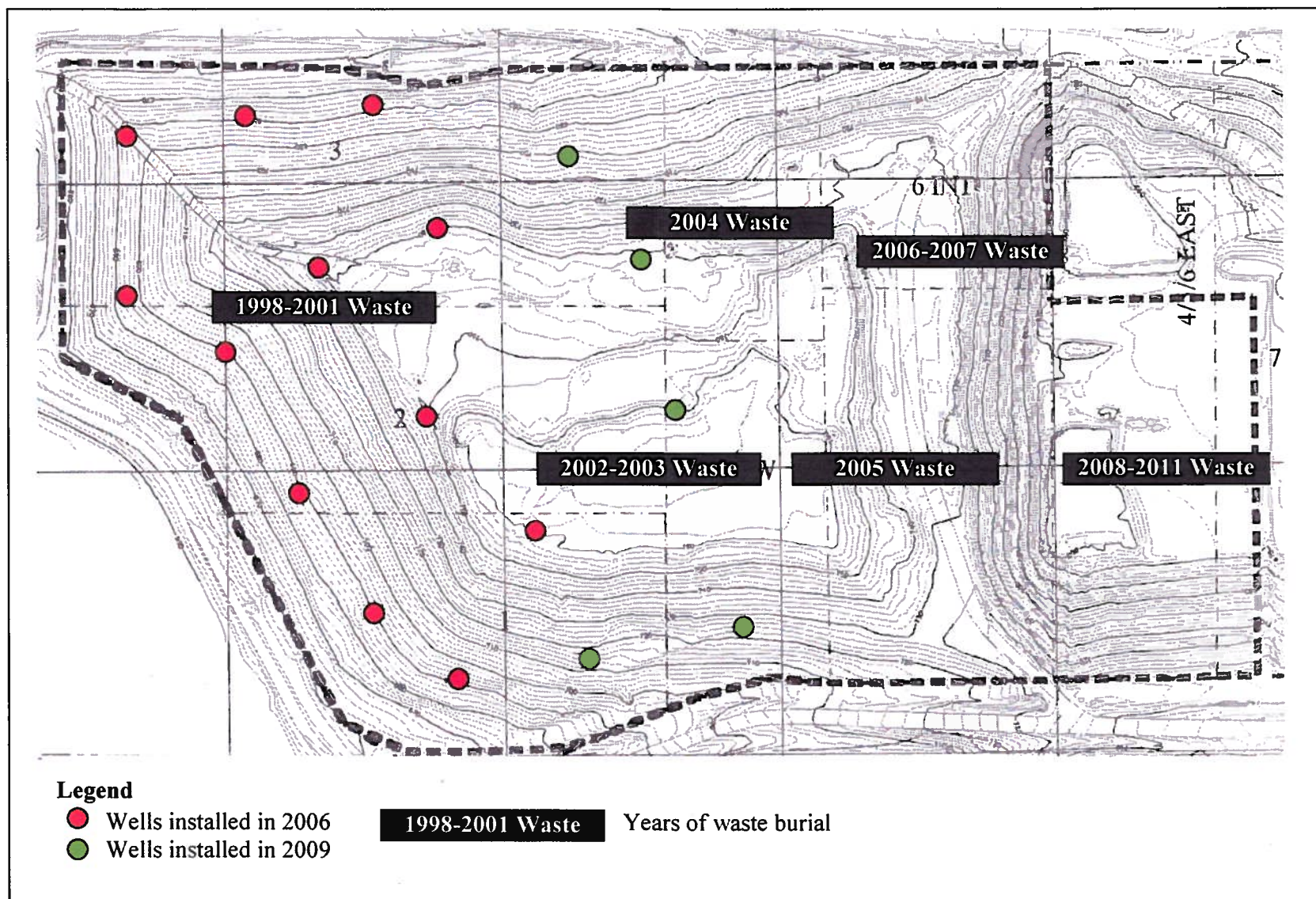


Figure S7. Location of waste disposal and schedule of final cover and GCCS installation at Landfill Q.

Table S7. Estimates of Monthly Collection Efficiency ( $\alpha_{ji}$ ) from 2006 through 2011 for Gas Generated at Landfill Q (%)<sup>a</sup>

Gas recovery period	Years of waste burial					
	1998-2001	2002	2003	2004	2005	2006-2011
01/06 – 06/06	0	0	0	0	0	0
07/06 – 06/09	75	20	20	20	20	0
07/09 – 12/11	75	75	60	60	60	0

- a. Collection efficiency was estimated using expert judgment based on cover type, and the schedule of waste placement and GCCS installation. For gas generated from the waste mass accepted in 2003 and 2004, low collection efficiencies were assumed due to a low density of well coverage. Well installation events occurred in 2006 and 2009, respectively, as shown in Figure S7. Gas collection wells were assumed to be effective in July of the well installation year, as the explicit dates of well installations were not available.



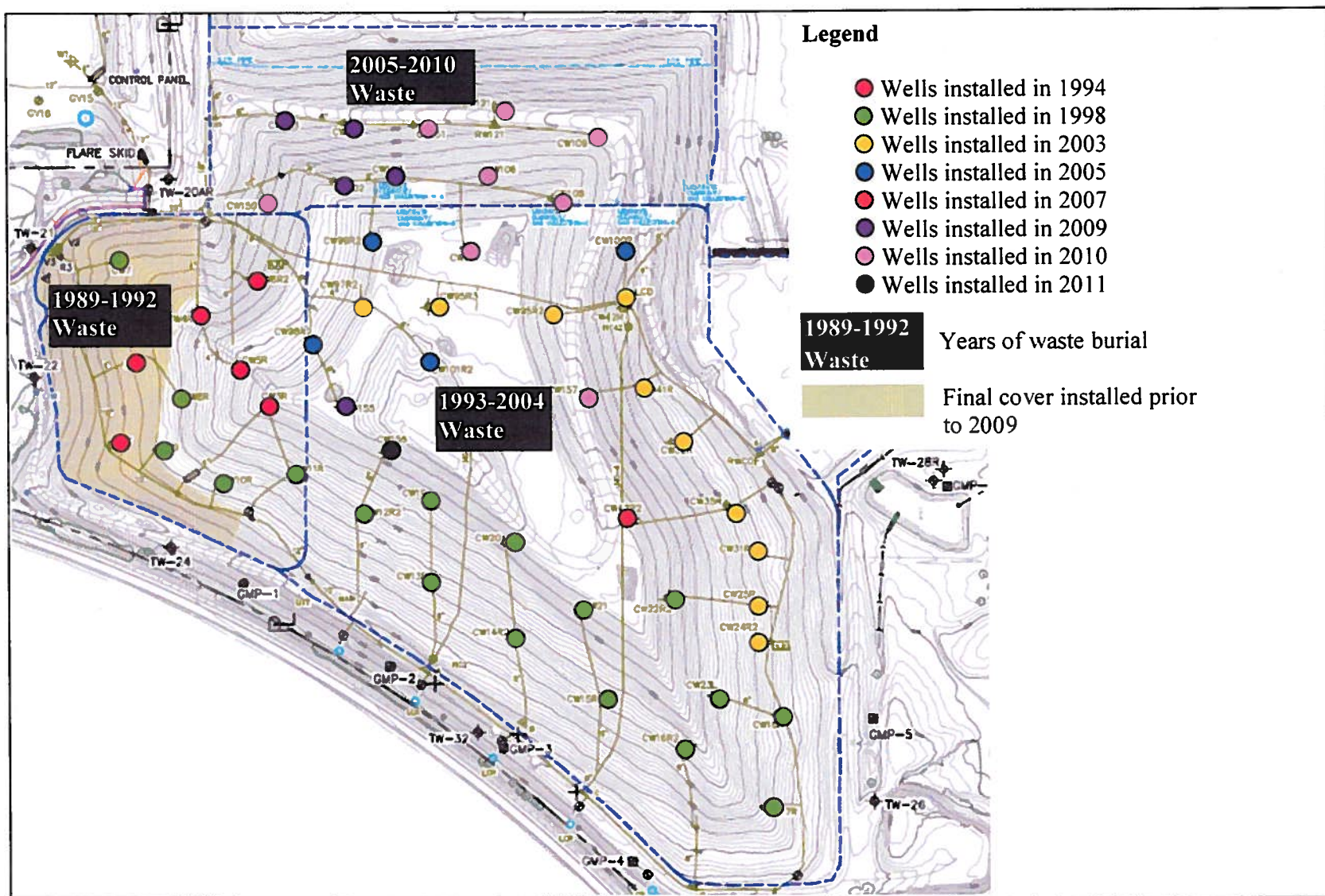


Figure S8. Location of waste disposal and schedule of final cover and GCCS installation at Landfill C2.

Table S8. Estimates of Monthly Collection Efficiency ( $\alpha_{ji}$ ) from 2009 through 2011 for Gas Generated at Landfill C2 (%)<sup>a</sup>

Gas recovery period	Years of waste burial								
	1989-1992	1993-2004	2005	2006	2007	2008	2009	2010	2011
01/09 – 06/09	90	75	0	0	0	0	0	0	0
07/09 – 06/10	90	75	40	40	40	0	0	0	0
07/10 – 12/10	90	75	40	40	40	40	40	0	0
01/11 – 06/11	90	75	60	60	60	40	40	0	0
07/11 – 12/11	90	75	60	60	60	40	40	40	0

- a. Collection efficiency was estimated using expert judgment based on cover type, and the schedule of waste placement and GCCS installation. For gas generated from the waste mass accepted after 2004, low collection efficiencies were assumed due to the low density of well coverage. Well installation events occurred in 2009, 2010, and 2011, respectively. Gas collection wells were assumed to be effective since July of the well installation year, as the explicit dates of well installations were not available.



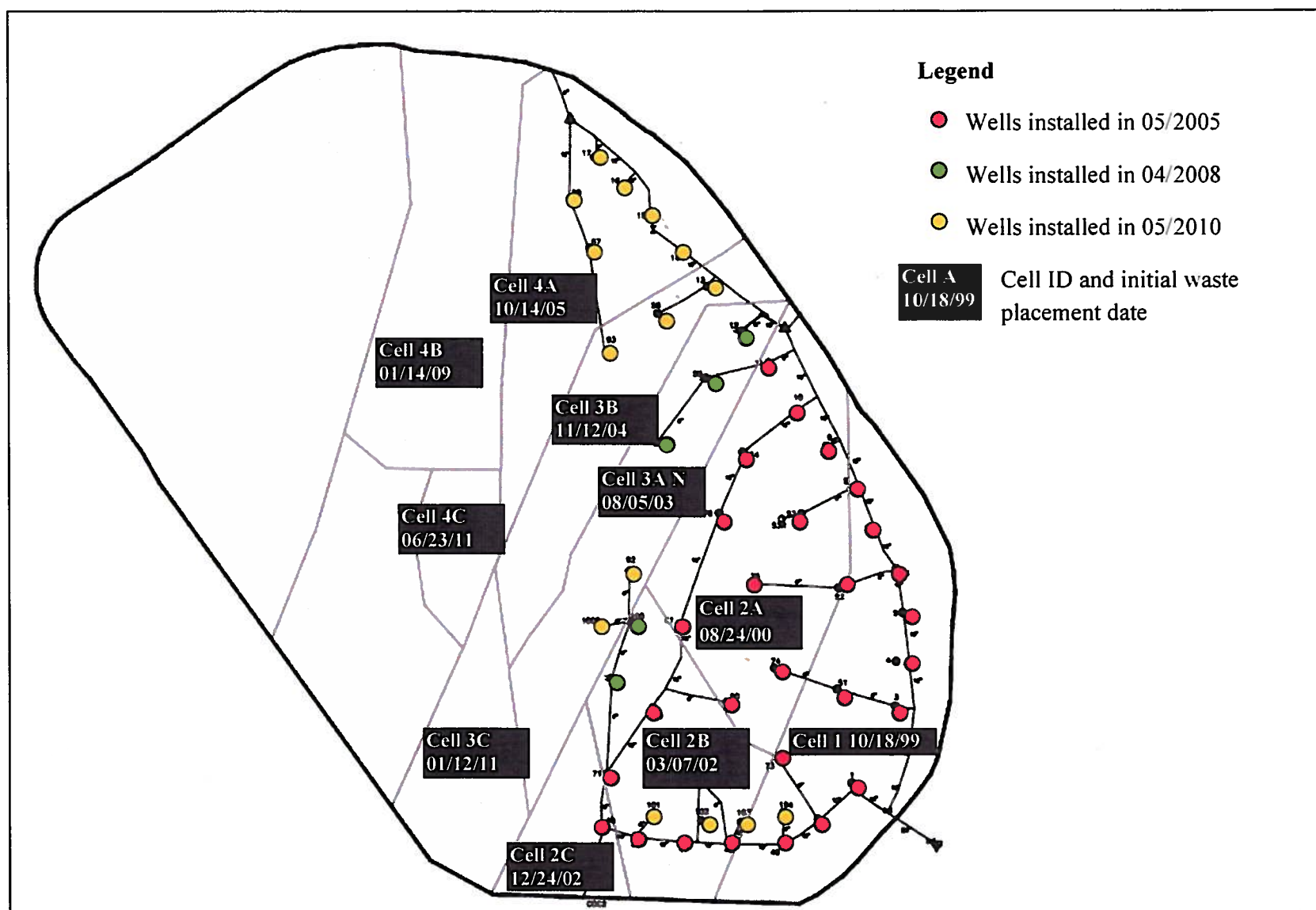


Figure S9. Location of waste disposal and schedule of final cover and GCCS installation at Landfill P2.

Table S9. Estimates of Monthly Collection Efficiency ( $\alpha_{ij}$ ) from 2006 through 2011 for Gas Generated at Landfill P2 (%)<sup>a</sup>

Gas recovery period	Years of waste burial											
	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
01/06 – 04/08	75	75	75	0	0	0	0	0	0	0	0	0
05/08 – 05/10	75	75	75	60	60	0	0	0	0	0	0	0
06/10 – 12/11	75	75	75	75	75	50	50	50	50	0	0	0

- a. Collection efficiency was estimated using expert judgment based on cover type, and the schedule of waste placement and GCCS installation. For gas generated from the waste mass accepted after 2004, low collection efficiencies (50%) were assumed due to the low density of well coverage.

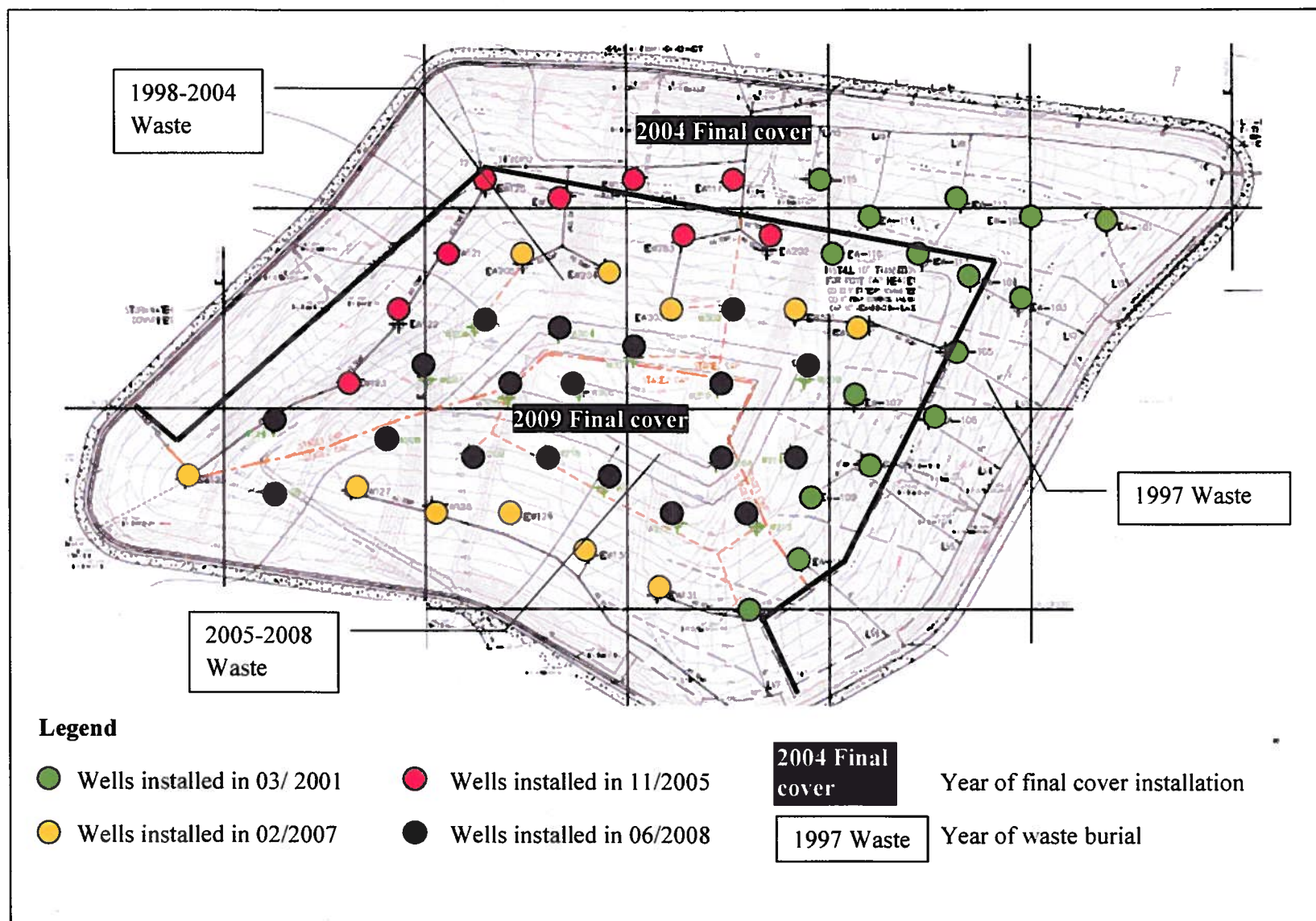


Figure S10. Location of waste disposal and schedule of final cover and GCCS installation at Landfill N.

Table S10. Estimates of Monthly Collection Efficiency ( $\alpha_{ji}$ ) from 2005 through 2011 for Gas Generated at Landfill N (%)<sup>a</sup>

Gas recovery period	Years of waste burial							
	1986-1996	1997	1998-2003	2004	2005	2006	2007	2008
01/05 – 12/05	80	90	0	0	0	0	0	0
01/06 – 02/07	80	90	60	20	0	0	0	0
03/07 – 06/08	80	90	75	60	60	60	0	0
07/08 – 06/09	80	90	85	75	75	75	75	60
07/09 – 12/11	80	90	90	90	90	90	90	90

- a. Collection efficiency was estimated using expert judgment based on cover type, and the schedule of waste placement and GCCS installation. Wastes accepted between 1986 and 1996 were placed in an unlined area of this facility (not shown in Figure S10). A relatively low collection (80%) was assumed for the gas generated from this portion of the waste mass since 2006, although the waste mass is capped under the final cover.

Table S11. Estimate of Methane Yield for Wood Waste

Wood type	Methane yield <sup>a</sup> (mL CH <sub>4</sub> g <sup>-1</sup> )	Aggregated wood types to match composition data	Percent of wood in mixed wood waste <sup>a</sup> (%)	Average methane yield (mL CH <sub>4</sub> g <sup>-1</sup> )
Hardwood (HW) - Red Oak	33.3	Lumber (HW and SW)	58.3	10.3 <sup>b</sup>
HW - Eucalyptus	0	PW	22.2	6.3
Softwood (SW) - Spruce	7.5	OSB	8.3	44.4 <sup>c</sup>
SW - Radiata Pine	0.5	MDF and PB	11.1	5.1 <sup>d</sup>
Oriented Strand Board (OSB) - HW	88.8	Average methane yield for mixed wood waste		11.7
OSB - SW	0			
Plywood (PW)	6.3			
Particleboard (PB)	5.6			
Medium density fiberboard (MDF)	4.6			

a. Adopted from reference 1.

b. Average methane yield for the four hardwoods and softwoods measured.

c. Average of hardwood and softwood OSB.

d. Average of MDF and PB.

Table S12. Estimate of Methane Yield for Bulk MSW<sup>a</sup>

	Moisture (fraction of total wt.)	Methane yield (mL CH <sub>4</sub> dry g <sup>-1</sup> )	U.S. average	CA	DE	FL	GA	IA	KS	MN	OR	PA	WS
Textiles	0.10	46.4	4.2	3.1	3.3	4.6	4.2	5.9	11.0	2.8	3.8	4.3	3.5
Wood	0.10	11.7 <sup>b</sup>	7.3	0.4	0.3	N/A	2.0	N/A	6.8	7.7	5.0	2.8	2.5
Food waste	0.70	300.7	17.7	19.0	12.1	9.7	12.6	12.7	9.5	12.8	19.4	13.7	14.5
Yard trimmings	0.39	72.0	7.1	8.5	8.5	12.2	2.8	1.6	8.0	2.4	7.8	5.9	1.7
Miscellaneous organics	0.40	128.1	0.2	5.7	3.2	N/A	1.3	1.8	N/A	1.4	2.4	3.0	2.9
Newspaper	0.06	74.3	0.9	2.9	4.4	5.6	5.1	4.8	4.6	4.2	2.7	4.7	2.8
Office paper	0.06	217.3	4.3	2.6	2.4	5.5	3.6	2.9	6.4	3.2	2.2	4.1	2.0
Mixed paper	0.06	145.8	2.9	4.8	3.9	N/A	6.7	8.3	N/A	8.8	8.0	5.3	7.1
Glossy paper	0.06	84.4	0.9	1.0	2.0	N/A	2.8	2.2	3.6	2.6	1.6	3.0	1.4
OCC/Kraft bags	0.05	152.3	5.7	8.8	10.2	8.5	11.6	10.2	17.2	7.1	4.0	9.5	6.0
Composite/miscellaneous	0.06	132.1	9.3	7.4	10.5	15.0	13.3	11.1	7.7	11.6	9.4	13.4	12.5
Calculated methane yield <sup>c</sup>			55.7	63.3	61.3	62.1	71.2	67.0	71.0	64.0	61.0	71.1	58.9

a. Adopted from reference 2.

b. Adopted from Table S11.

c. Methane yield was calculated on a wet basis. The unit is mL CH<sub>4</sub> wet g<sup>-1</sup>, which is equivalent to m<sup>3</sup> CH<sub>4</sub> wet Mg<sup>-1</sup>.

d. N/A = not available.

Table S13. Estimate of Weighted Average First Order Waste Decay Rate ( $k$ )

Landfill	Waste-in-place, Mg <sup>a</sup>	Fraction of cumulative waste mass placed in 11 landfills, %	$k$ , yr <sup>-1</sup>
S	1,425,570	2.1	0.12
G	4,484,675	6.6	0.10
H	1,981,344	2.9	0.15
T	28,729,729	42.6	0.04
C1	5,224,091	7.7	0.17
P1	4,301,015	6.4	0.04
M	6,112,009	9.1	0.17
Q	1,693,606	2.5	0.13
C2	2,829,063	4.2	0.15
P2	5,142,714	7.6	0.09
N	5,517,278	8.2	0.11
Weighted average $k$			0.09 (0.12) <sup>b</sup>
Std. dev.			0.05 (0.04) <sup>b</sup>

- Waste-in-place represents the cumulative mass of biodegradable waste in place over the period for which gas collection data were available.
- The values in parentheses exclude Landfill T in the estimate.

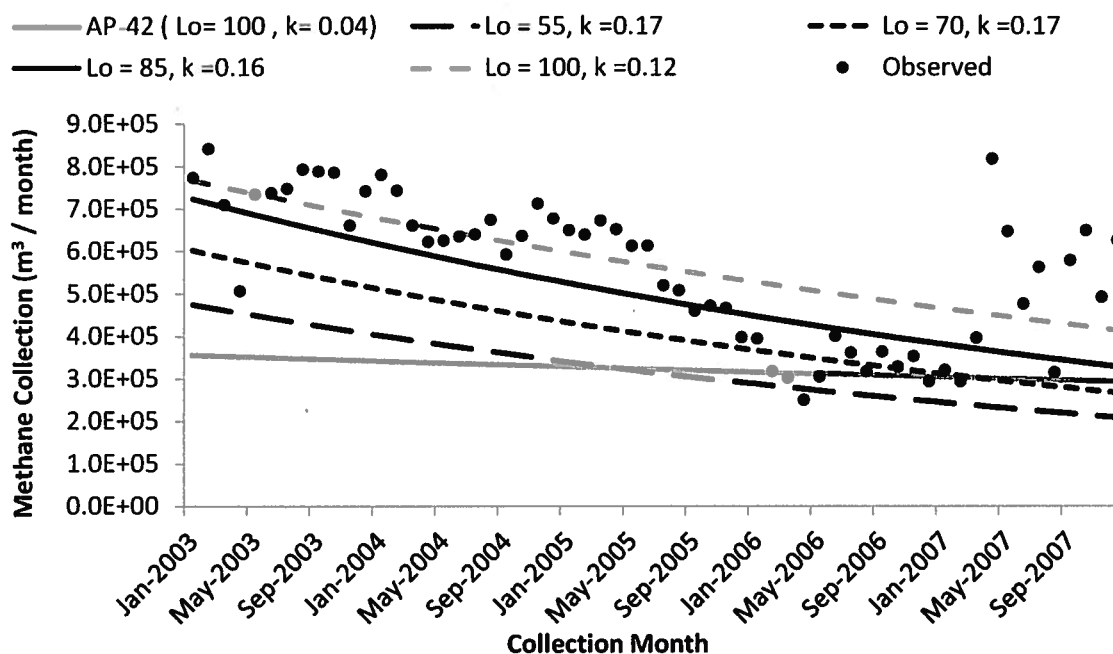


Figure S11. Observed methane collection from Landfill S versus estimates produced with different LandGEM parameterizations. The model was constrained to the  $L_0$  values given in the legend and the accompanying  $k$  is the value determined by minimizing the sum of squared errors.

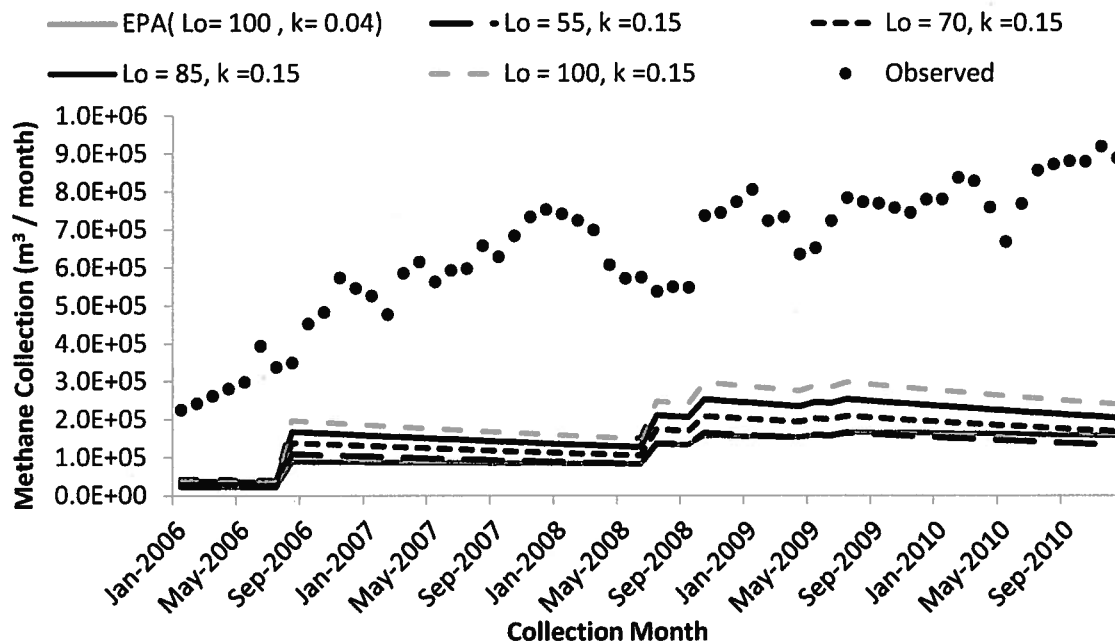


Figure S12. Observed methane collection from Landfill H versus estimates produced with different LandGEM parameterizations. The model was constrained to the  $L_0$  values given in the legend and the accompanying  $k$  is the value determined by minimizing the sum of squared errors.



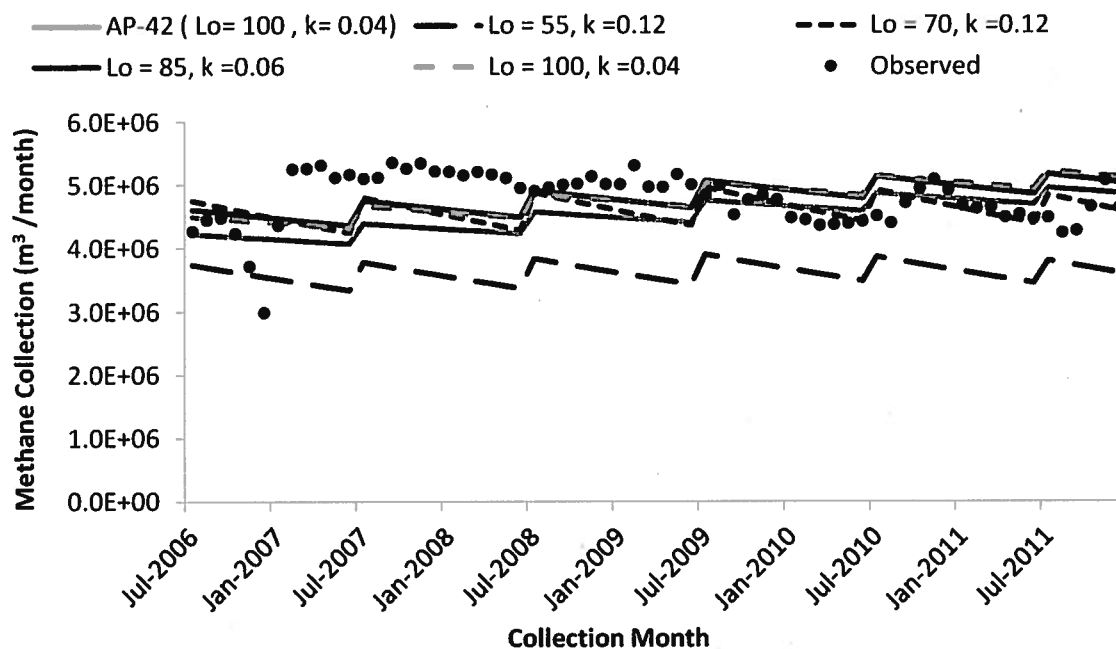


Figure S13. Observed methane collection from Landfill T versus estimates produced with different LandGEM parameterizations. The model was constrained to the  $L_0$  values given in the legend and the accompanying  $k$  is the value determined by minimizing the sum of squared errors.

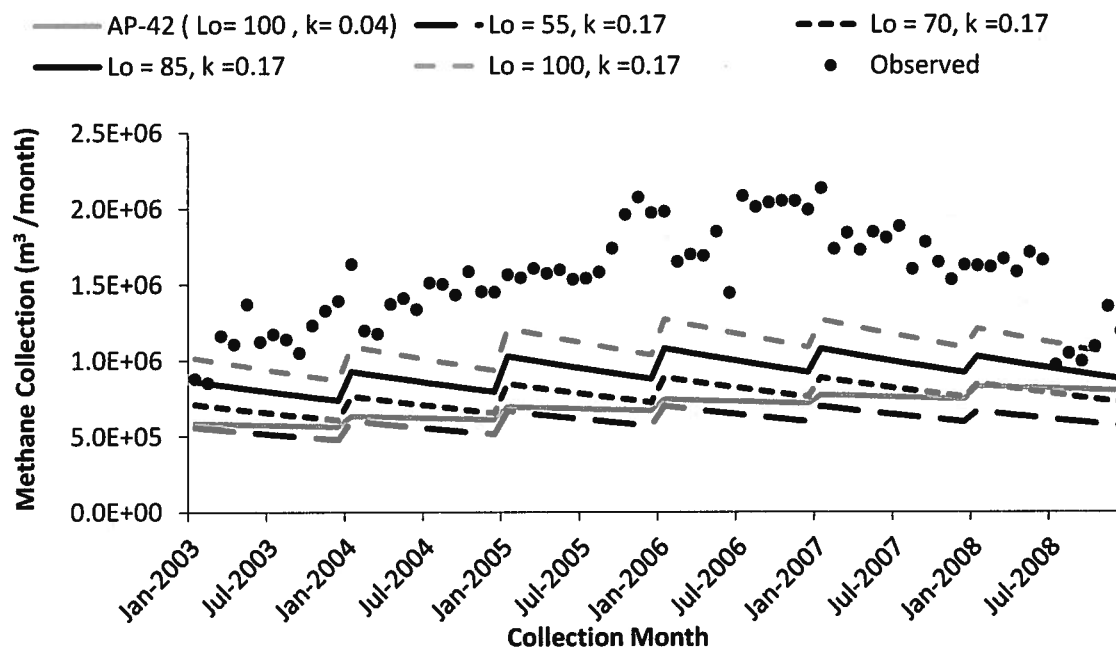


Figure S14. Observed methane collection from Landfill C1 versus estimates produced with different LandGEM parameterizations. The model was constrained to the  $L_0$  values given in the legend and the accompanying  $k$  is the value determined by minimizing the sum of squared errors.

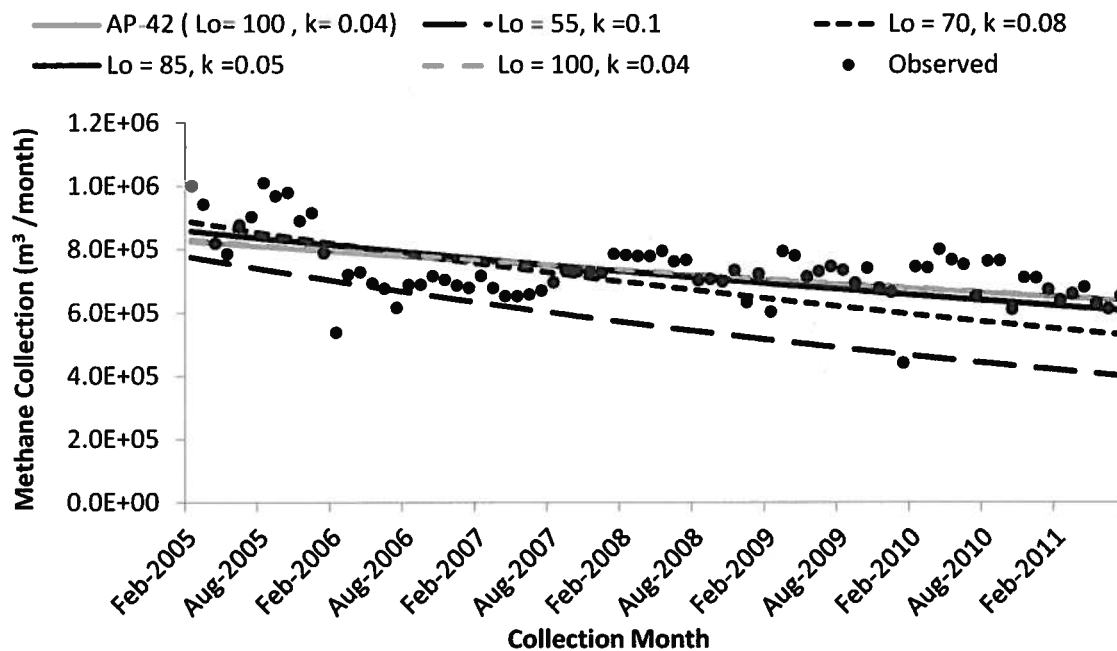


Figure S15. Observed methane collection from Landfill P1 versus estimates produced with different LandGEM parameterizations. The model was constrained to the  $L_0$  values given in the legend and the accompanying  $k$  is the value determined by minimizing the sum of squared errors.

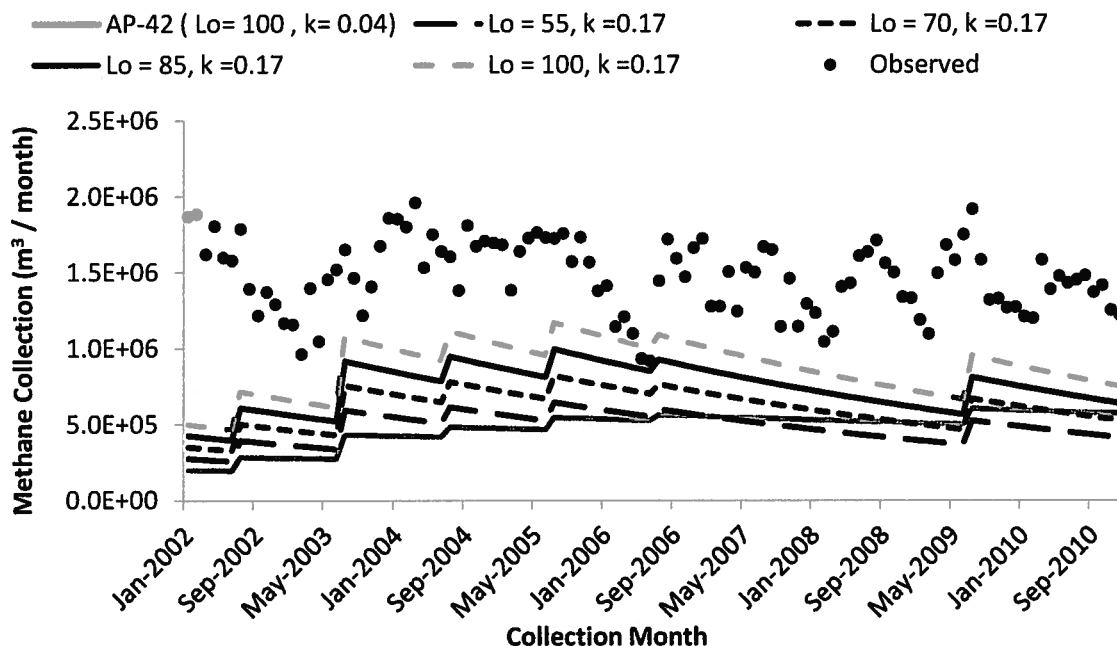


Figure S16. Observed methane collection from Landfill M versus estimates produced with different LandGEM parameterizations. The model was constrained to the  $L_0$  values given in the legend and the accompanying  $k$  is the value determined by minimizing the sum of squared errors.

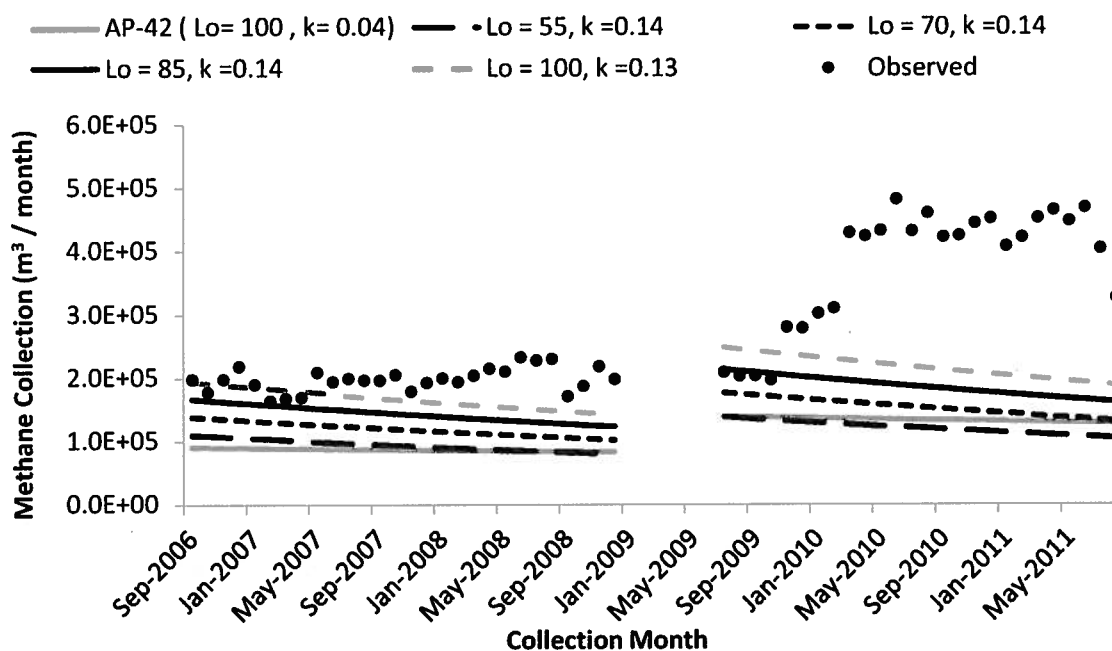


Figure S17. Observed methane collection from Landfill Q versus estimates produced with different LandGEM parameterizations. The model was constrained to the  $L_0$  values given in the legend and the accompanying  $k$  is the value determined by minimizing the sum of squared errors.

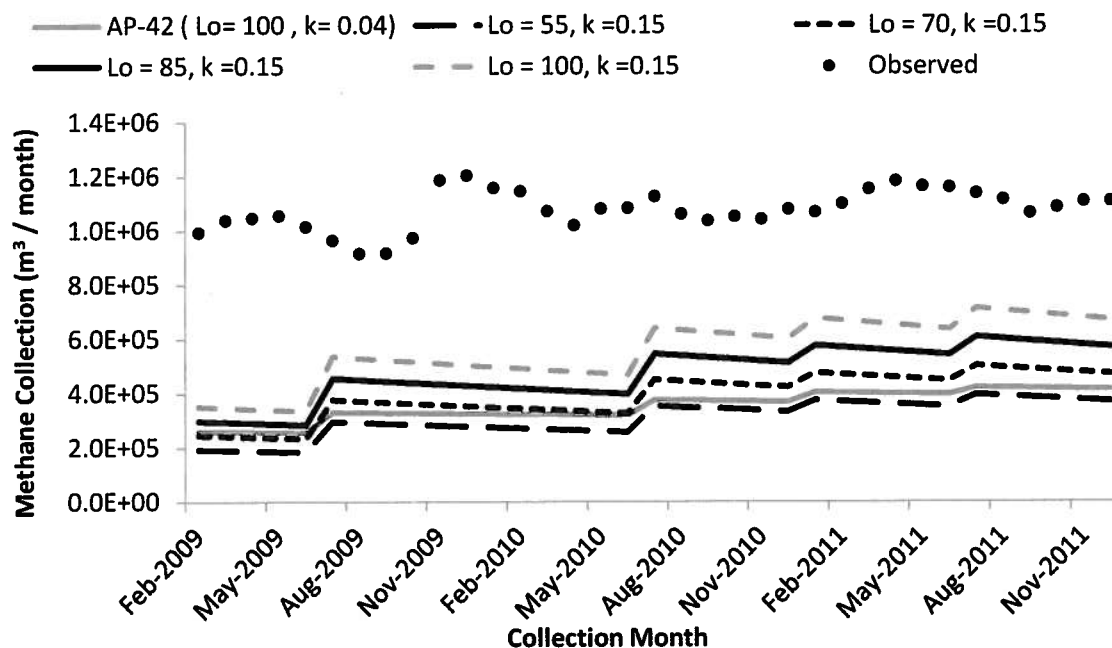


Figure S18. Observed methane collection from Landfill C2 versus estimates produced with different LandGEM parameterizations. The model was constrained to the  $L_0$  values given in the legend and the accompanying  $k$  is the value determined by minimizing the sum of squared errors.

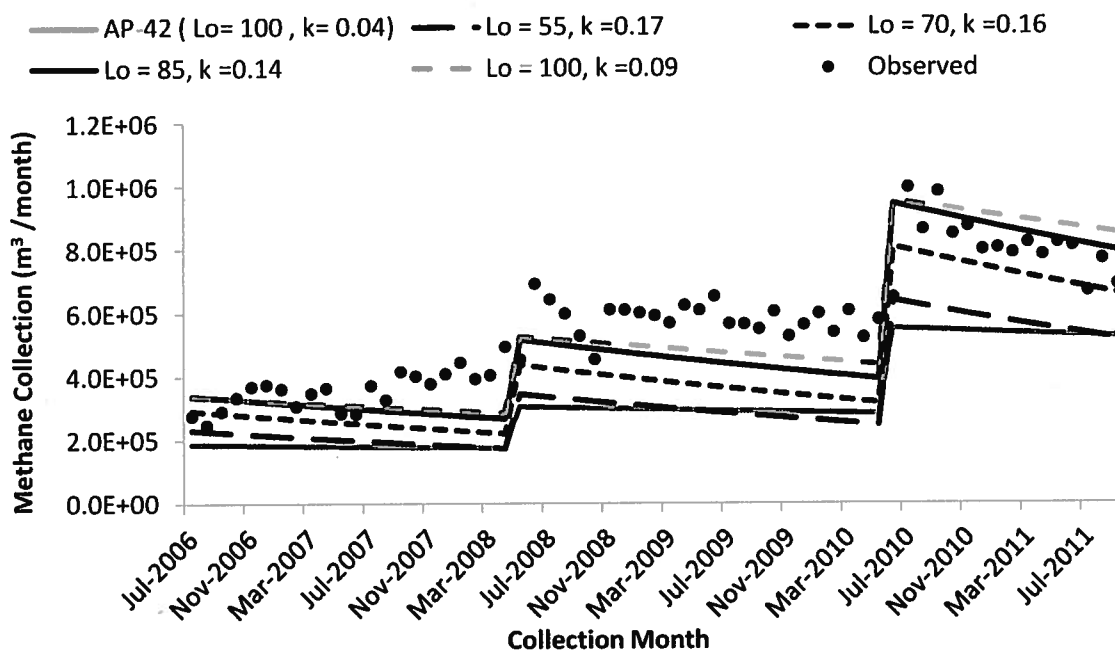


Figure S19. Observed methane collection from Landfill P2 versus estimates produced with different LandGEM parameterizations. The model was constrained to the  $L_0$  values given in the legend and the accompanying  $k$  is the value determined by minimizing the sum of squared errors.

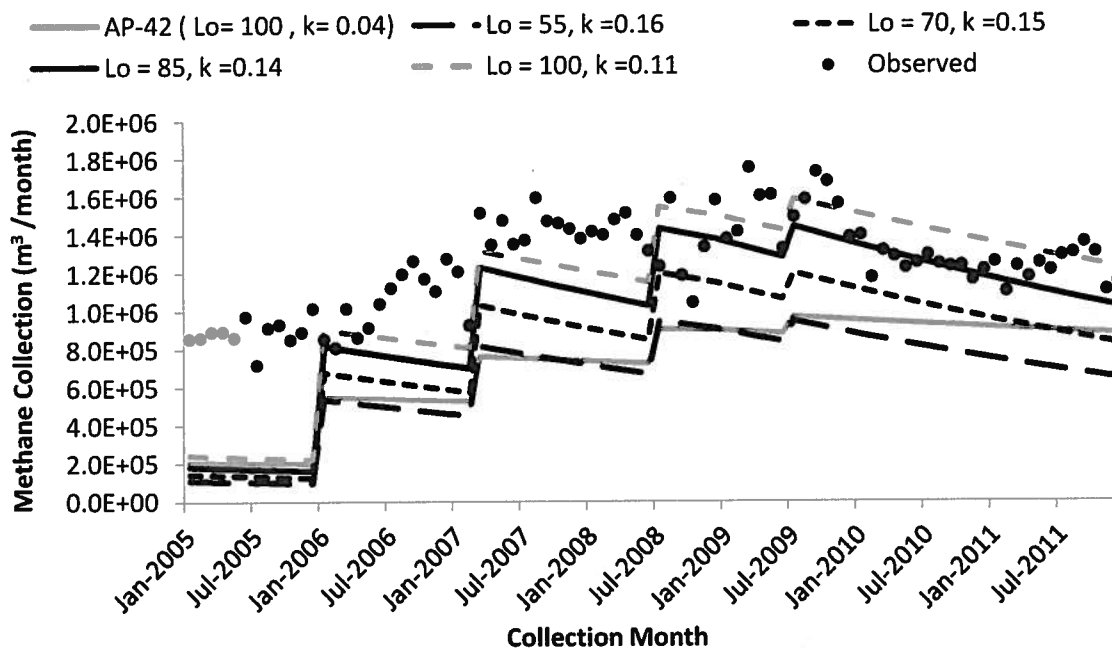


Figure S20. Observed methane collection from Landfill N versus estimates produced with different LandGEM parameterizations. The model was constrained to the  $L_0$  values given in the legend and the accompanying  $k$  is the value determined by minimizing the sum of squared errors.

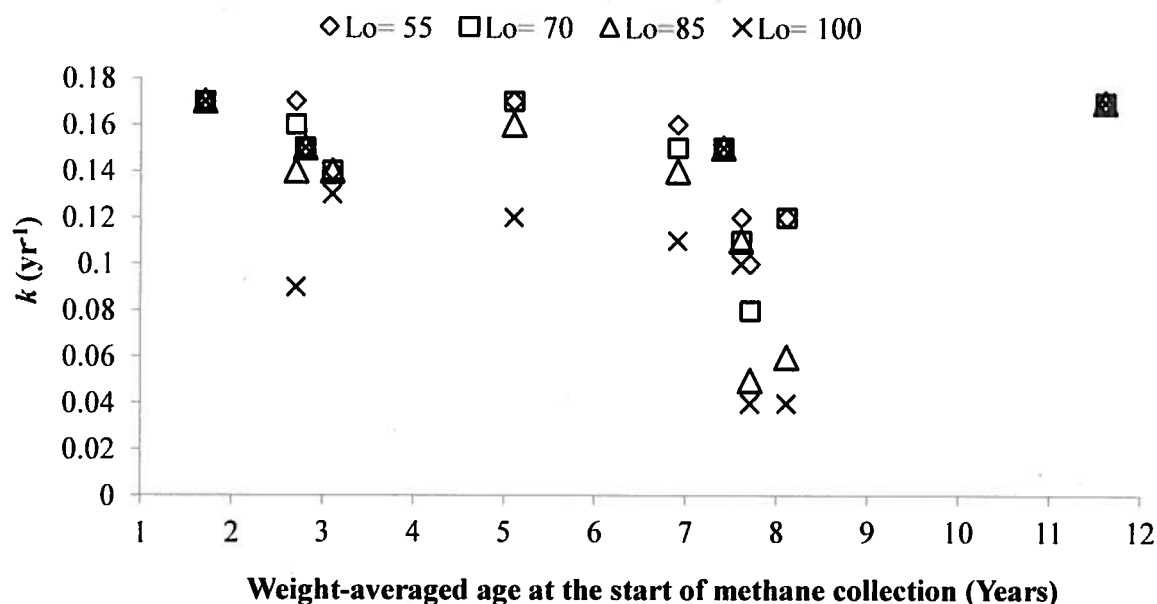


Figure S21. Optimal  $k$  values at various  $L_0$  ( $\text{m}^3 \text{CH}_4 \text{ wet Mg}^{-1}$ ) scenarios versus weight-averaged age at the start of methane collection. The absence of a clear trend suggests that the low bias in estimated  $k$  did not have a noticeable influence on the results.

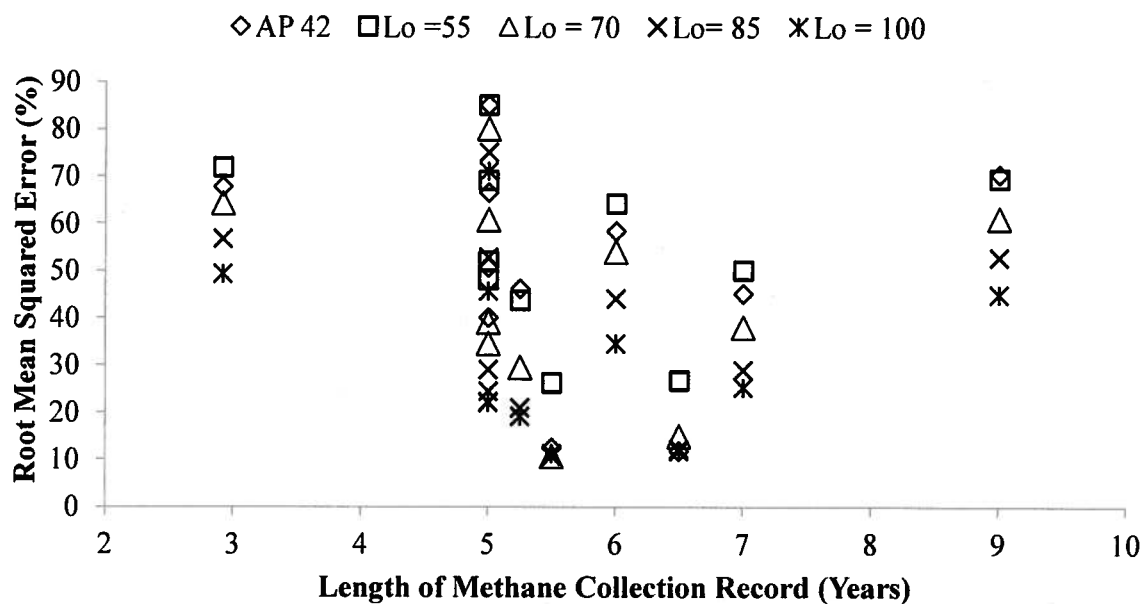


Figure S22. Root Mean Squared Error (RMSE) versus the length of the methane collection record at each of the 11 landfills. Although a longer collection record could result in a more accurate fit, this does not appear to be the case, as there is no observed correlation.



## References

- (1) Wang, X.; Padgett, J.M.; De, I.C.; Barlaz, M.A. Wood Biodegradation in Laboratory-Scale Landfills. *Environ. Sci. Technol.* **2011**, *45*, 6864-6871.
- (2) Staley, B.,F. and Barlaz, M.,A. Composition of Municipal Solid Waste in the United States and Implications for Carbon Sequestration and Methane Yield. *J. Environ. Eng.* 2009, *135*, 901-909.

# Performance of North American Bioreactor Landfills. II: Chemical and Biological Characteristics

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**Abstract:** The objective of this research was to examine the performance of five North American bioreactor landfills. This paper represents the second of a two-part series and addresses biological and chemical aspects of bioreactor performance including gas production and management, and leachate chemistry. The data support accelerated methane generation at several landfills ( $k = 0.08\text{--}0.21$  1/year) relative to the AP-42 default decay rate ( $k = 0.04$  1/year). While the data indicate that gas collection increases at bioreactor landfills, a general relationship between decay rate and moisture added or wet weight water content could not be identified. There was no indication that gas collection increases appreciably when the water content reaches 40%. Most of the leachates at the landfills in this study were commingled from cells operating as a bioreactor and conventionally. Nevertheless, trends in pH and BOD:COD in the bioreactor leachates were consistent with the impacts of enhanced biological activity. Ammonia concentrations also increased over time but remained below levels reported to be inhibitory. For both heavy metals and speciated organic chemicals, there was no indication that bioreactor landfill leachate is significantly different from leachate generated at conventional landfills.

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**CE Database subject headings:** Landfills; Reactors; Solid wastes; Methane; Chemical treatment; Biological processes.

**Author keywords:** Landfills; Bioreactor; Solid waste; Leachate quality; Methane.

## Introduction

This paper represents the second of a two part series to examine the performance of bioreactor landfills in North America. Numerous advantages are attributed to the operation of a landfill as a

bioreactor including accelerated biological decomposition that leads to (1) more rapid settlement that ultimately reduces land requirements for waste disposal and (2) higher rates of gas production that improve the feasibility of recovering the gas for beneficial use. Bioreactor landfills also provide for in situ leachate treatment as degradable organic matter in the leachate is consumed within the waste mass. Finally, the enhanced rate of decomposition may reduce the time and intensity of postclosure monitoring and maintenance.

The objective of this research was to evaluate monitoring data from five North American landfills that are operated as bioreactors to determine the extent to which the data support the advantages described above. For this study, a landfill was considered to be operated as a bioreactor if specific design features had been incorporated to facilitate leachate recirculation, and there was a concerted effort to operate the landfill to accelerate decomposition.

The companion paper (Bareither et al. 2010) focuses on physical characteristics including landfill hydrology and settlement. This paper addresses biological and chemical aspects of bioreactor performance, including the collection and management of landfill gas (LFG), as well as leachate chemistry. Following a brief description of the study sites, this paper examines methane recovery data, followed by an analysis of leachate chemistry including the biological oxygen demand (BOD), chemical oxygen demand (COD), pH, and ammonia as well as metals and speciated organic compounds.

## Site Descriptions

The five landfills studied and the criteria by which they were selected are described in the accompanying manuscript (Bareither

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et al. 2010). Briefly, the landfills include two in the mid-Atlantic region (M and D), one each in central and western Pennsylvania (G and L) and one in the west (Y). The five include three public entities and two private sector landfills. The area of each landfill that was operated as a bioreactor varied from 1.4 to 40 ha.

## Methane Generation

### Data Analysis

Gas collection data from each landfill were analyzed to evaluate whether there is evidence to quantify the extent to which methane generation is accelerated in bioreactor landfills relative to conventional landfills. Methane recovery is typically modeled using the U.S. EPA's LandGem model (U.S. EPA 2005)

$$Q_n = kL_0 \sum_{i=0}^n \sum_{j=0.0}^{0.9} \frac{M_i}{10} e^{-k \cdot t_{i,j}} \quad (1)$$

where  $Q_n = \text{CH}_4$  collection rate ( $\text{m}^3\text{-CH}_4/\text{year}$ ) in year  $n$ ;  $M_i$  = mass of waste accepted (Mg) in year  $i$ ;  $L_0$  = ultimate methane yield ( $\text{m}^3\text{-CH}_4/\text{Mg}$ );  $k$  = decay rate (1/year);  $j$  = deci-year time increment; and  $t$  = time (year). AP-42 default values for  $k$  and  $L_0$  for conventional landfills are 0.04 1/year and 100  $\text{m}^3\text{-CH}_4/\text{year}$  (U.S. EPA 1998).

### Data Analysis Methodology

The decay rate in Eq. (1) was estimated from gas collection data for Landfills D, G, and Y but not for Landfills L and M, where gas collection data were not measured separately in sections of the landfill operated as a bioreactor. Decay rate optimizations for Landfills D and G were executed in EXCEL using the Solver function. Historic waste filling data were input into the LandGEM model for individual cells at D and G. LandGEM was modified to predict methane recovery rates that corresponded to the identical elapsed times as were recorded for the physical methane collection measurements. All recorded methane collection data were used in the optimization procedures, except in the expansion cell at G. In this case, the decay rate was optimized for the data recorded following installation of 14 additional gas wells as discussed below. Two constraints were used in the optimization procedure, both incorporating the residuals of the methane recovery data (i.e., predicted less measured). The primary constraint involved varying the decay rate for a given  $L_0$ , such that the sum of squared residuals was minimized. The secondary constraint forced the sum of residuals to zero so to limit bias in the optimization procedure.

The gas data for landfill Y were unique as the cells were filled and covered quickly so that most of the gas produced was collected and the mass of refuse did not change once gas collection began. This allowed for a more thorough analysis of decay rate. Cumulative collectable methane can be calculated from Eq. (2) which is the integrated form of Eq. (1)

$$V = L_0 M (1 - e^{-kn}) \quad (2)$$

where  $V$  = cumulative  $\text{CH}_4$  collected from beginning of life to time  $t$  ( $\text{m}^3$ );  $M$  = initial mass of refuse (Mg); and other terms are as in Eq. (1). Eq. (2) can be arranged as in Eq. (3), where the numerator on the right side is the remaining methane potential at time  $t$

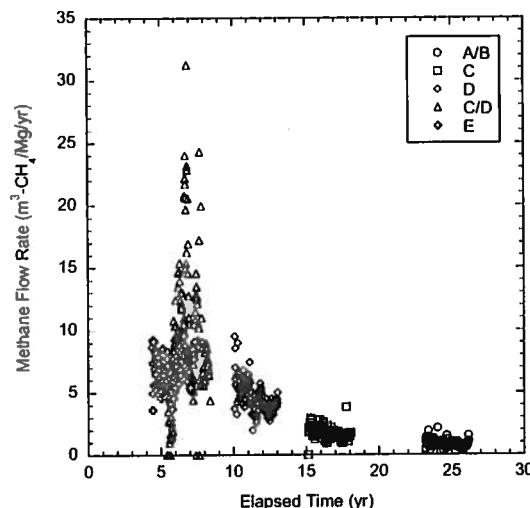


Fig. 1. Methane flow rate for the five cells at Landfill D

$$-kt = \ln \left( \frac{L_0 - V/M}{L_0} \right) \quad (3)$$

The decay rate is then calculated by linear regression at an assumed  $L_0$  and the measured  $V$ .

To estimate  $k$  based on methane collection that occurred after the onset of recirculation, some adjustments to the data from Landfill Y were required.  $L_0$  was reduced by the volume of gas estimated to have been produced prior to initiation of gas collection ( $V_{uc}$ ) and for the volume of gas produced prior to the initiation of recirculation ( $V_{dry}$ ).  $V_{uc}$  was estimated using Eq. (1) with  $k=0.04$  1/year and several different values of  $L_0$  as presented with the results, while  $V_{dry}$  was measured. All decay rate optimizations were performed at the AP-42 default of 100  $\text{m}^3\text{-CH}_4/\text{Mg}$  to reflect regulatory considerations, as well as at 59  $\text{m}^3\text{-CH}_4/\text{Mg}$  which was estimated from published data on the composition of waste discarded in landfills (Staley and Barlaz 2009).

### Results of Decay Rate Analysis

#### Landfill D

The LFG extraction system at Landfill D consisted of either perforated vertical wells (Areas C, D) or combined horizontal gas collection/leachate injection trenches (Areas C/D valley, E). Gas extraction flows were recorded daily using meters at each cell, as well as with a flow meter located at the flare station. The gas flow from each cell was scaled to match the total flow at the flare, which resulted in an average correction of 16.6%. The final cover consisted of either clay or an exposed geomembrane, except for Cell E, which was still active and did not have a final cover.

Although active gas extraction began at Landfill D in August 1996, LFG collection rates were only measured from individual cells after November 2003. Measured methane collection rates for all cells are presented in Fig. 1. Data are presented as a function of elapsed time after first waste placement to provide a parameter that is more specific than the calendar year, but does not require estimates of waste age as such estimates would increase uncertainty in subsequent interpretation. The performance of Cell A/B has been described elsewhere (Morris et al. 2003) and was included in Fig. 1 to illustrate gas generation from relatively old refuse.

**Table 1.** First-Order Decay Rates, Area of Individual Cells, and Liquid Addition for the Study Sites

Landfill	Cell	First-order decay rate (1/year) <sup>a</sup>	Area of cell (m <sup>2</sup> )	Total liquid added to waste (L) <sup>b</sup>	Mass of waste (Mg)	Liquid added/landfill area (L/m <sup>2</sup> or mm)	Liquid added/Mg-MSW (L/Mg) <sup>c</sup>	Water content (%) <sup>d</sup>
D	A/B	0.14 (0.09)	110,100	81,804,072	642,050	743	127	61
	C	0.17 (0.08)	78,500	15,645,735	15,645,735	199	28	33
	D	0.12 (0.12)	91,100	15,430,601	515,193	169	30	44
	C/D	0.15 (0.15)	— <sup>e</sup>	7,897,461	109,769	—	72 (204)	44
	E	0.08 (0.17)	131,600	13,803,445	1,001,455	105	14 (76)	51
G	Original	0.05 (0.11)	306,556	19,080,732	5,302,531	62	4	42
	Expansion	0.09 (0.22)	306,758	505,220,520	6,970,213	1,647	72 (195)	49
Y	NE	0.15 (0.35)	14,200	26,987,075	69,240	1,900	383 (419)	31
	W	0.09 (0.17)	24,300	26,527,810	176,240	1,092	151 (264)	27

<sup>a</sup>First value was calculated at  $L_0=100 \text{ m}^3\text{-CH}_4/\text{Mg}$  and the value at  $L_0=59 \text{ m}^3\text{-CH}_4/\text{Mg}$  is given parenthetically.

<sup>b</sup>Total liquid added includes all methods of recirculated leachate (i.e., well, trench, pond, and surface application), as well as supplemental liquids for Landfill Y.

<sup>c</sup>Liquid added per mass of waste affected for recirculation in horizontal trenches is given parenthetically (see companion paper).

<sup>d</sup>Computations based on water balance for Landfills D and Y; physical water content analysis for Landfill G.

<sup>e</sup>Area of Cell C/D could not be determined since this cell sits in a valley and does not have a defined base area.

Estimates of decay rate for each cell are summarized in Table 1. In all cases, the estimated decay rate at  $L_0$  of  $100 \text{ m}^3\text{-CH}_4/\text{Mg}$  exceeds the AP-42 default value of 0.04 1/year. The decay rate for Area E is lowest, possibly because this is an active cell and the gas collection efficiency varied with time as new collection trenches were activated. In addition, Area E has received less liquid than the other cells (Table 1). Relationships between decay rate,  $L_0$ , and liquid addition are discussed below.

#### Landfill Y

The gas collection system at Landfill Y included both horizontal trenches and vertical wells. For the NE cell, horizontal collection lines were installed between each of the four waste lifts and directly under the reinforced polypropylene geomembrane cover. For the W cell, horizontal collection lines were installed between Lifts 2 and 3, Lifts 3 and 4, and on top of Lift 4. There has been some flooding of the horizontal trenches, and most of the gas has been collected from vertical wells and the permeable layer at the top.

Methane collection rates for Landfill Y are presented in Fig. 2 and decay rates are summarized in Tables 1 and 2. As for Landfill D, decay rates for Landfill Y are greater than the AP-42 default. In all cases,  $V_{uc} + V_{dry}$  was less than 5% of the assumed  $L_0$ , suggesting that the analysis was not highly sensitive to the estimate of  $V_{uc}$ . The higher decay rate in the NE cell is consistent with the higher normalized liquid addition relative to the W cell.

#### Landfill G

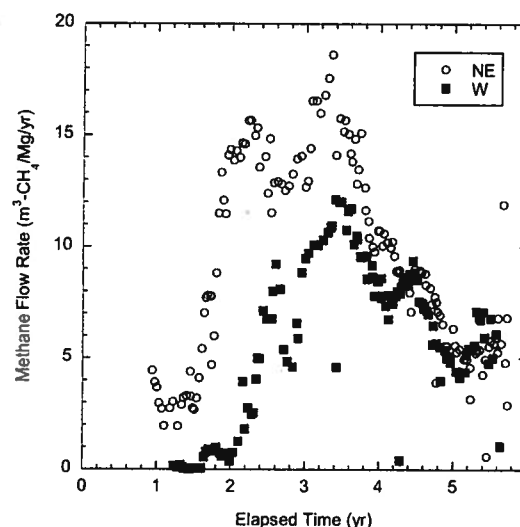
Separate gas collection data were available for the original and expansion cells that were operated from 1986 to 2003 and 2000 to the present, respectively (Fig. 3). Gas was collected from vertical wells only in the original cell and from both horizontal trenches and vertical wells in the expansion cell. The same trenches are used for leachate injection, and gas is only collected after the trenches have drained. The sharp increase in gas collection following Year 6 in the expansion landfill (Fig. 3) is concurrent with the installation of 14 additional gas wells and the decay rate was estimated based on the data after installation of these wells. In the original landfill, the methane collection rate began to decrease approximately 6 months after the cessation of refuse burial. As

presented in Table 1, the estimated decay rates for the original and expansion areas are above 0.04 1/year. The higher decay rate in the expansion area is consistent with the higher recirculation rate.

#### Summary of Methane Generation Rate Data

A summary of the estimated decay rates for each landfill as well as information on the cell area and quantity of liquid added to the refuse are presented in Table 1. The results support the supposition that refuse decomposition can be accelerated at full-scale landfills that are operated as bioreactors, as the estimated first-order decay rates are all greater than the AP-42 default of 0.04 1/year. This contrasts with an earlier study in which the gas data were not sufficient to document enhanced decomposition at four of five bioreactor landfills (Benson et al. 2007).

Decay rates were calculated at multiple  $L_0$ s to emphasize the sensitivity of the estimated decay rate to the assumed  $L_0$  as well

**Fig. 2.** Methane flow rate for the NE and W cells at Landfill Y

**Table 2.** Estimates of Decay Rate ( $k$ ) for Different Values of  $L_0$  at Landfill Y

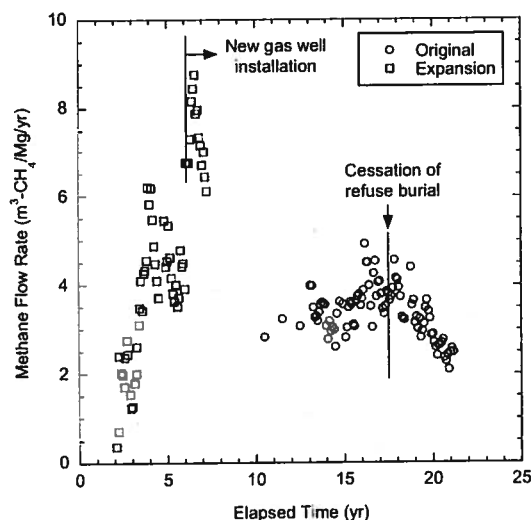
$L_0$ description	Assumed $L_0$ ( $\text{m}^3\text{-CH}_4/\text{Mg}$ )	NE cell		W cell	
		$V_{\text{nc}}/M$ ( $\text{m}^3/\text{Mg}$ )	$k$ (1/year)	$V_{\text{nc}}/M$ ( $\text{m}^3/\text{Mg}$ )	$k$ (1/year)
AP-42 default	100	2.8	0.15	1.9	0.09
120% of AP-42 default	120	3.4	0.12	2.3	0.07
80% of AP-42 default	80	2.2	0.21	1.5	0.12
Measured from Landfill Y pilot bioreactor cell <sup>a</sup>	88	2.5	0.18	1.7	0.11

<sup>a</sup>Pilot cell was operated in the mid-1990s and the waste received was similar to that in the W and NE cells (Yazdani et al. 2006).

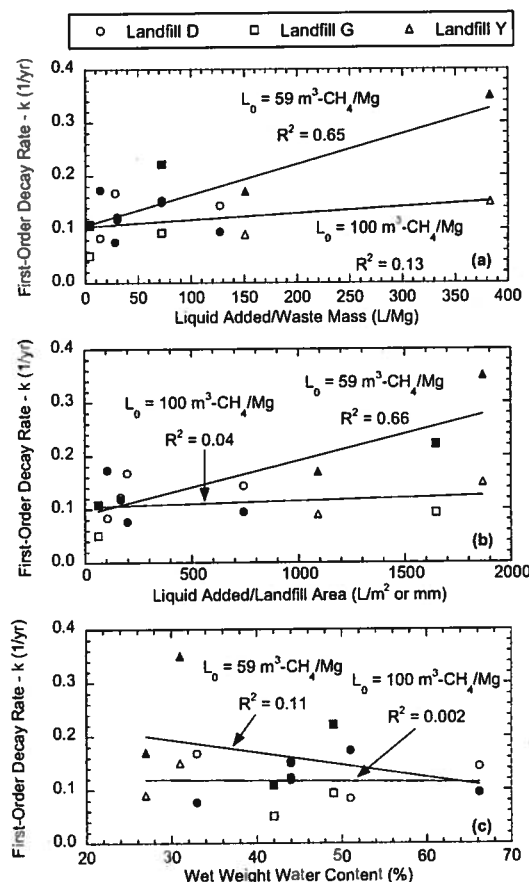
as the uncertainty in  $L_0$  (Tables 1 and 2). The decay rate calculated at  $L_0 = 100 \text{ m}^3\text{-CH}_4/\text{Mg}$  is significant from a regulatory perspective as this is the AP-42 default. Recognizing that most field-scale gas collection data are confounded by temporally varying gas collection efficiency is important. This alone adds some uncertainty to the estimated decay rate. The AP-42 defaults to which the results in this study were compared were developed from gas collection data at landfills that were believed to have high collection efficiencies. Nonetheless, the actual gas collection efficiency is unknown and likely varied between the landfills used to construct the AP-42 database and the landfills evaluated in this study. Given the inherent uncertainties in gas modeling, small differences in  $k$  between landfills probably are not significant.

Relationships between  $k$  and the ratio of liquid added per mass of waste, ratio of liquid added per landfill area, and the average wet weight moisture content at Landfills D, G, and Y are presented in Fig. 4. The data show a modest trend of increasing  $k$  with increasing liquid addition on a gross waste mass [Fig. 4(a)] and gross area [Fig. 4(b)] basis. In both Figs. 4(a and b), the slope is only significantly different from zero ( $p < 0.05$ ) for the decay rates calculated at  $L_0 = 59 \text{ m}^3\text{-CH}_4/\text{Mg}$ . Even so, the coefficients of determination ( $R^2$ ) are low, and the data are insufficient to propose a general trend. There is no apparent relationship between  $k$  and wet weight water content [Fig. 4(c)].

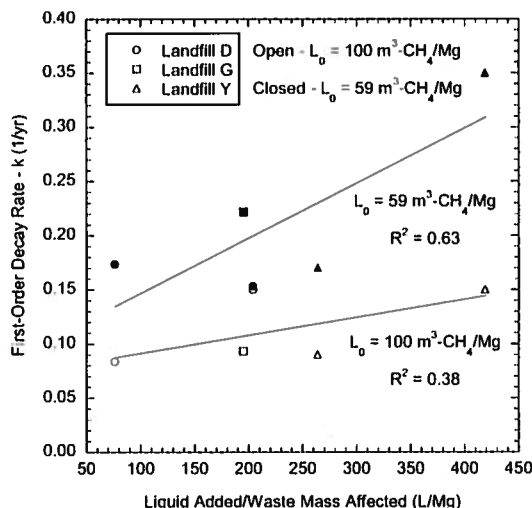
The absence of a trend between  $k$  and water content is likely due to the difficulty in estimating the water content via water balance computations, and the variability in physical water content measurements from excavated solids. In water balance com-

**Fig. 3.** Methane flow rate for the original and expansion cells at Landfill G

putations, assumptions of initial water content, runoff versus infiltration, and infiltration from precipitation after capping can all lead to errors in the estimated water content. When the water content is measured from refuse samples, the heterogeneity of water content in the varying material fractions of waste (Hull et al. 2005), as well as uneven wetting due to channelized flow, can lead to a wide range of water contents over the lateral and vertical dimensions of a landfill (see companion paper). Moreover, when water is added via trenches or wells, the moisture content of the refuse varies with distance from the point of application, whereas

**Fig. 4.** Relationship between first-order decay rate and (a) liquid added per mass of waste; (b) liquid added per landfill area; and (c) wet weight water content for individual cells at Landfills D, G, and Y. Data points represent individual cells at each landfill. The open and closed symbols represent  $L_0 = 100$  and  $L_0 = 59 \text{ m}^3\text{-CH}_4/\text{Mg}$ , respectively. The slope is only significantly different from zero for  $L_0 = 59$  in (a) and (b).





**Fig. 5.** Relationship between first-order decay rate and liquid added per mass of waste affected in horizontal recirculation trenches for those landfill cells with horizontal trenches installed during waste filling. Data points represent individual cells at each landfill. The regression at  $L_0=59$  is only significant at the 89% confidence level.

the calculated moisture content used in Fig. 4(c) represents even distribution. As demonstrated in the companion manuscript, even a bioreactor cell likely has refuse at varying moisture contents. Interestingly, U.S. regulations impose gas collection requirements based on the time at which a bioreactor landfill reaches a water content of 40% (U.S. EPA 2003). Given that the trends in Fig. 4 are modest to nonexistent, other metrics might be more appropriate.

An additional analysis was conducted for landfills where leachate was recirculated in horizontal trenches. For this analysis, the liquid added per unit mass of waste was computed as described in the companion paper using the wetted areas in Haydar and Khire (2005). These wetted areas represent the cross-sectional area of waste that is wetted during leachate injection in horizontal trenches, and were derived from numerical simulations in HYDRUS-2D. The relationships in Fig. 5 have a more well-defined trend and less scatter than those in Fig. 4. This is most likely due to more accurate estimates of the waste wetted by the trench and the more uniform application of moisture in a landfill deliberately constructed for leachate recirculation. However, the slope at  $L_0=59 \text{ m}^3\text{-CH}_4/\text{Mg}$  in Fig. 5 is only significant at  $p=0.11$ , which is due in part to the small number of data points. Interestingly, in no case was a relationship significant at  $L_0=100 \text{ m}^3\text{-CH}_4/\text{Mg}$ .

The range of decay rates estimated in this study is lower than the rate of 0.3 1/year suggested in Faour et al. (2007), which is applicable only to optimum conditions in cells operated as bioreactors from the start. However, there are numerous differences between this study and Faour et al. (2007), including the range of data sets used, the aggregation of data from multiple landfills, the allowance of a lag phase, and model fits in which both  $k$  and  $L_0$  were allowed to vary in Faour et al. (2007). For full-scale landfills that received waste over many years, a condition present at Landfills D and G, Faour et al. (2007) estimated decay rates between 0.11 and 0.21 1/year, which is comparable to, but somewhat higher than the  $k$  estimated for Landfills D (0.08–0.17) and G (0.05–0.09) using  $L_0=100 \text{ m}^3\text{-CH}_4/\text{Mg}$ . Recently, Tolaymat et al. (2010) estimated decay rates for the Outer Loop, Kentucky

bioreactor of 0.11 1/year for a site specific  $L_0=54.8 \text{ m}^3\text{-CH}_4/\text{Mg}$ . Given the numerous variables affecting gas collection, such variation between studies is expected.

## Leachate Quality

Leachate composition is the most common mechanism for monitoring a landfill. The analysis presented here includes bulk parameters (pH, COD, BOD,  $\text{NH}_3\text{-N}$ ), selected heavy metals, and selected trace organic chemicals. The bulk parameters are analyzed first, followed by analysis of heavy metals and speciated organics.

### Landfill M

Leachate from the bioreactor and control areas at Landfill M was collected separately. Nonetheless, direct comparisons of leachate quality are inappropriate because (1) the waste ages are different as refuse burial in the bioreactor cell was completed in August 1995, 42 months before the control cell and (2) leachate from the entire landfill was stored in a leachate tank and then recirculated to the bioreactor. Thus, the 10.7-ha bioreactor received an input stream that reflects leachate quality from the 164-ha landfill.

There were no apparent trends with time for BOD:COD, pH, and  $\text{NH}_3\text{-N}$  concentrations and averages are presented in Table 3. The average BOD:COD in the bioreactor cell was less than in the control cell ( $p<0.05$ ), and the leachate tank also exhibited a relatively low BOD:COD even though leachate collected from newer cells, where higher BOD:COD would be expected, was included in the tank. The pH was above 6.7 in both cells and the leachate tank throughout the monitoring period. pH in the control cell was significantly higher ( $p<0.05$ ) than in the bioreactor cell, which may be a result of the significantly higher  $\text{NH}_3\text{-N}$  concentration in the control cell leachate relative to the bioreactor cell.

Although the data neither support nor refute the hypothesis that BOD:COD stabilizes more rapidly in bioreactor cells, the data do support the hypothesis that biodegradable organic matter can be degraded in situ in a bioreactor landfill. A low BOD:COD was maintained in the bioreactor leachate despite the dosing with leachate from the entire landfill.

### Landfill L

Leachate from the entire landfill (18.6 ha) is collected in a tank at Landfill L and then recirculated in Area C (8.1 ha), which has received leachate via trenches and surface application since 2001. Leachate data are available for two cells in Area C and a tank that receives leachate from the entire landfill. Leachate recirculation was interrupted from April 2004 to January 2005 to facilitate installation of a final cover on some slopes in Area C.

The pH in Area C increased from about 6 in 1996 to about 7 prior to the initiation of recirculation in 2001, and varied between 6.5 and 7.8 with no apparent trend until 2005, when the pH began to decrease [Fig. 6(a)]. The leachate tank pH has been consistently higher than the bioreactor cell leachate, suggesting the contributions of more basic pH from older parts of the landfill. The closer agreement of the tank and bioreactor leachate pH since 2003 likely reflects the reduced leachate contributions from other parts of the landfill. BOD was not measured so BOD:COD cannot be considered. Average COD concentrations for the leachate tank and Area C are presented in Table 3.

Ammonia concentrations [Fig. 6(b)] appear to be increasing,

**Table 3.** Leachate Characteristics for the Studied Landfills

Landfill	Cell	n	pH			n	BOD:COD			n	NH <sub>3</sub> -N (mg/L)		
			Mean (SD) <sup>a</sup>	Minimum	Maximum		Mean (SD) <sup>a</sup>	Minimum	Maximum		Mean (SD) <sup>a</sup>	Minimum	Maximum
M	Conventional	10	7.50 (0.21)	7	7.7	25	0.21 (0.22)	0	0.87	25	1,736 (472) <sup>b</sup>	383	2,630 <sup>b</sup>
	Bioreactor	10	6.99 (0.24)	7	7.5	27	0.10 (0.08)	0	0.4	25	339 (80)	84	450
	Tank	5	7.7 (0.26)	7.5	8.2	14	0.14 (0.16)	0	0.6	14	1,257 (296)	520	1,590
Y	W	22	6.93 (0.24)	6.5	7.5	19	0.09 (0.05)	0	0.25	22	210 (240)	9.5	850
	NE	23	7.49 (0.24)	7	8.2	21	0.13 (0.19)	0	0.8	23	343 (307)	13.5	1,420
G	—	76	6.81 (0.66)	5.6	8.1	55	0.45 (0.28)	0	1	58	379 (282)	13	1,250
L	Cells 1 and 2	71	6.77 (0.51)	5.4	7.8	71	1,866 (1743) <sup>d</sup>	140	11,000	70	308 (220)	2.5	790
	Cells 1 and 2 LDS <sup>c</sup>	40	7.04 (0.5)	6.1	9	41	1,093 (1102) <sup>d</sup>	62	6,520	41	310 (247)	3.6	756
D	Cell C	213	7.03 (0.52)	4.8	8.2	209	0.31 (0.25)	0	1	213	281.2 (122.3)	1	585
	Cell D: PCS1	158	6.65 (0.5)	4.7	7.4	151	0.33 (0.30)	0	0.98	157	344 (166)	<0.1	735
	Cell D: PCS2	132	6.51 (0.42)	5.1	7.4	121	0.55 (0.21)	0	0.97	132	210 (135)	0.13	537
	Cell E	90	6.43 (0.36)	5.4	7.2	80	0.43 (0.20)	0.1	0.83	87	159 (139)	0.25	488

<sup>a</sup>Data are the average for all samples with the standard deviation presented parenthetically.

<sup>b</sup>One outlier value of 8,760 mg/L was excluded from the mean.

<sup>c</sup>Leachate detection system.

<sup>d</sup>Data are COD (mg/L) as BOD was not measured.

but are within the range of typical landfill leachate (Kjeldsen et al. 2002). Concentrations in the bioreactor leachate are higher than concentrations in the leachate tank toward the end of the record, which may be indicative of enhanced protein hydrolysis and subsequent ammonia release to leachate due to stimulation of biological activity.

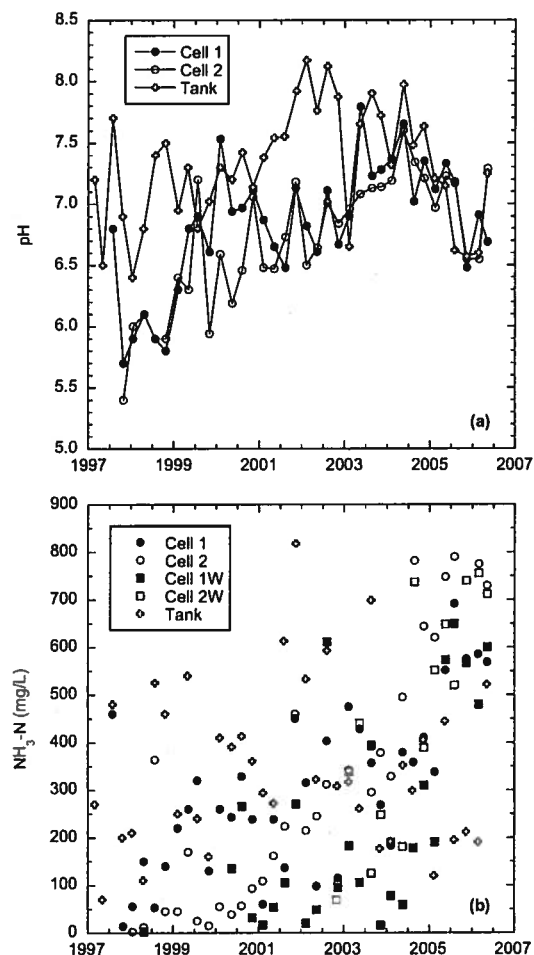
Ammonia has been detected in the leak detection system (LDS) on several occasions, and mean concentrations of ammonia and COD in the leachate and LDS are comparable (Table 3). This suggests the liquid in the LDS described in the companion paper represents leakage through the upper liner (geomembrane).

### Landfill D

Leachate was monitored separately from Areas C, D, C/D Valley, and E at Landfill D. Leachate from the entire landfill was stored in two 2.8 million-L tanks, and then added to the bioreactor areas over various periods. Thus, the recirculated leachate reflects leachate quality of the entire landfill. Area A/B had a relatively permeable cover over the period of the data set and therefore contributed a significant fraction of total leachate (69 to 40% between 1990 and 2006). The contribution from Area A/B decreased over time as the landfill area expanded.

pH, BOD:COD, and NH<sub>3</sub>-N data for each bioreactor cell are presented in Fig. 7. Data for two sumps (PCS1 and PCS2) are also presented. PCS1 includes leachate from Area D, the C/D Valley, and some of Area E, whereas PCS2 collects leachate from Area D and part of Area E. Because Area E is active, leachate in these sumps as well as the Area E data are influenced by fresh refuse. Leachate was recirculated through Year 7.5 in Area C, from Year 2 to the present in Area D, and from Year 6 to the present in Area E.

The pH was initially below 6 in all cells and required about 5 years to reach neutral (Fig. 7). This suggests that recirculation stimulated an accumulation of carboxylic acids. In Area C and Sump PCS1, the pH increase is consistent with a decrease in

**Fig. 6.** (a) pH; (b) ammonia concentration in Landfill L leachate

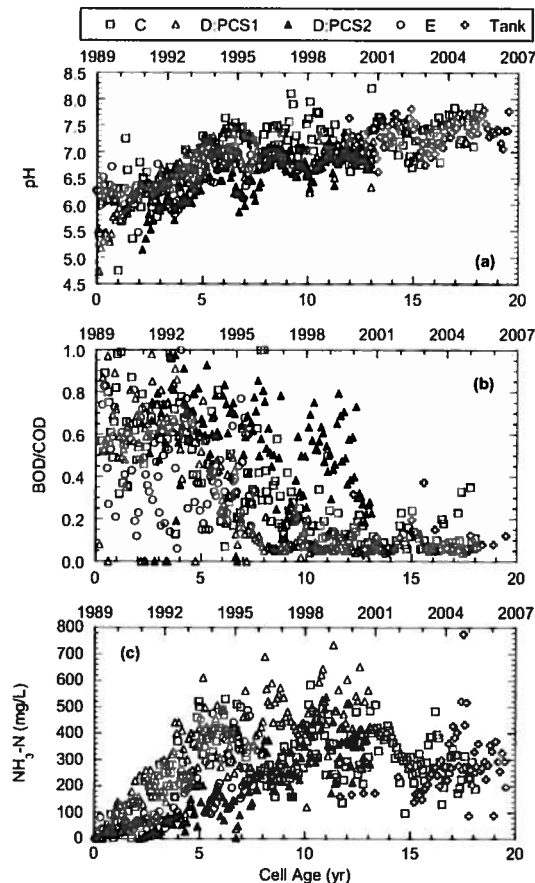


Fig. 7. (a) pH; (b) BOD:COD; and (c) and ammonia for Landfill D leachate. Date applies to leachate tank data.

BOD:COD, supporting the consumption of carboxylic acids. The pH decrease around Year 7 in PCS1 and 2 is consistent with a sharp increase in the volume of leachate being recirculated. While this suggests overstimulation of fermentative acid-producing bacteria, the pH recovered and again became neutral. The elevated BOD:COD in sump PCS2 leachate for nearly 10 years suggests a strong influence from fresh refuse.

There was a consistent increase in  $\text{NH}_3\text{-N}$  concentrations with age in all cells. The  $\text{NH}_3\text{-N}$  concentration appears to level off after 5 years in Areas C, E, and in Sump PCS1 and after 10 years in Sump PCS2.

### Landfill Y

Average leachate concentrations at Landfill Y are summarized in Table 3. The pH and  $\text{NH}_3\text{-N}$  concentrations in the NE and W cells are shown in Fig. 8. pH in both cells remained relatively constant except for an increase at Year 3 that coincides with a spike in  $\text{NH}_3\text{-N}$  [Fig. 8(b)]. There is no apparent explanation for the consistently higher pH in the NE cell.  $\text{NH}_3\text{-N}$  concentrations increased over time and then leveled off at about 400 mg/L in both cells. The increase in  $\text{NH}_3\text{-N}$  concentration in the NE cell occurred gradually, whereas a delay occurred in the W cell. There were no apparent trends in BOD:COD (data not shown). While the average pH was significantly lower in the W cell, there were no significant differences in the BOD:COD or  $\text{NH}_3\text{-N}$  concentra-

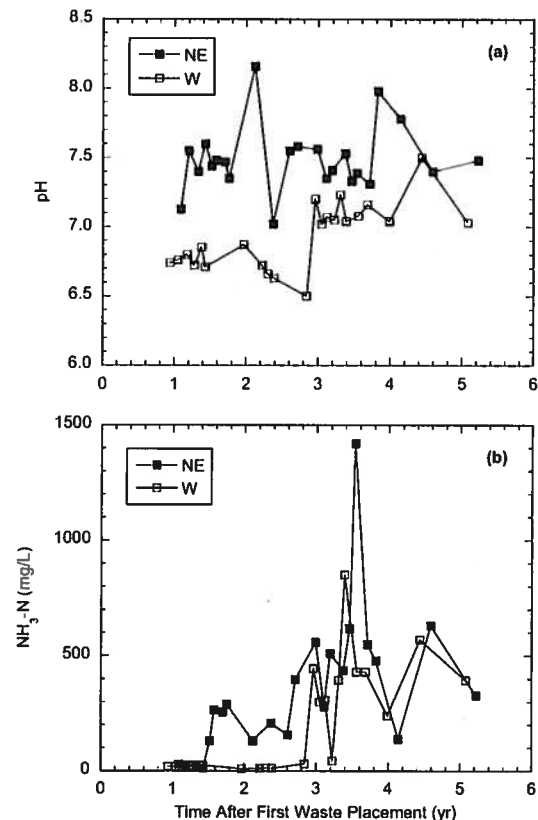


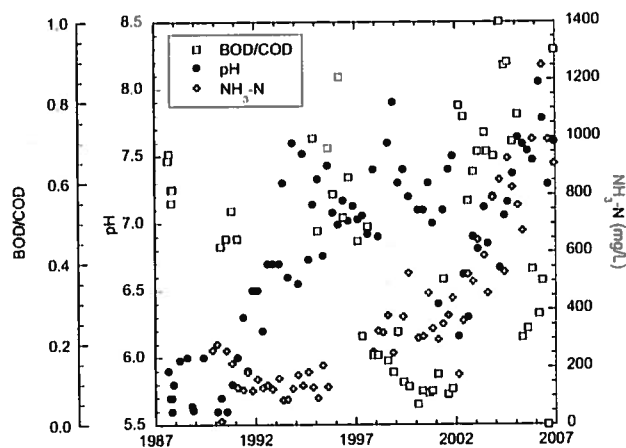
Fig. 8. (a) pH; (b) ammonia concentration in Landfill Y leachate

tion ( $p > 0.05$ ). The BOD:COD is relatively low in both cells ( $< 0.13$ ) and the leachate quality suggests actively decomposing refuse (Kjeldsen et al. 2002).

### Landfill G

Leachate quality at Landfill G represents a combination of leachate generated in the original and expansion landfills. For this reason, the data are graphed as a function of date as opposed to time since waste placement. Average leachate concentrations are summarized in Table 3 and trends are illustrated in Fig. 9.

Leachate in the original cell remained acidic for 6 years after burial before becoming neutral in 1993 (Fig. 9). No gas data were available prior to 1996. Thus, inhibition of gas production due to low pH could not be evaluated. The decrease in pH observed when the expansion landfill was started in 2000 suggests a significant influence of acidic leachate from fresh refuse, as was observed between 1987 and 1993 in the original cell. The low pH in 2000–2002 suggests that the initiation of recirculation stimulated fermentative activity (i.e., acid generation) and that the methanogenic archaea were unable to consume the acids as fast as they were generated. The BOD:COD decrease between 1993 and 1999 is consistent with a period when the pH increased to neutral. The sharp increase in the BOD:COD concurrent with the initiation of recirculation in the expansion landfill is consistent with the stimulation of fermentative activity described above. However, the BOD:COD increase occurs while the pH is increasing, which is atypical. Assuming that the BOD is attributable to carboxylic acids, this suggests a well buffered system. In contrast to the other landfills studied, Landfill G has an on-site wastewater treatment plant and receives a variety of other liquid wastes including



**Fig. 9.** pH, BOD:COD, and ammonia in Landfill G leachate. The expansion area opened in January 2000. Leachate recirculation began in the original and expansion areas in November 2000 and August 2001, respectively. Leachate recirculation was terminated in the original area in September 2003.

wastes from septic systems and powdered metal plants. The pH of the wastewater influent is often adjusted with a base that may provide a source of buffering atypical of landfill leachate.

$\text{NH}_3\text{-N}$  concentrations at Landfill G were relatively constant through 1996, but increased consistently thereafter (Fig. 9). This increase corresponds with the initiation of recirculation and the stabilizing of pH.

### Discussion of pH, BOD:COD, and Ammonia Concentrations

A number of factors impact leachate chemistry, including the quantity and intensity of infiltration, the presence of wastes other than municipal solid waste (MSW), and the degree to which leachate represents a specific landfill area and refuse age. The leachate represents different areas for each landfill studied. The leachate quality for Landfills D, M, and Y are distinct for each area, whereas the data for Landfills L and G represent a composite for the entire landfill. In addition, leachate is collected at the bottom of a landfill, and therefore reflects the state of decomposition in the lower layers. Specifically, if leachate from refuse in the acid phase percolates through well decomposed refuse, then this leachate likely reflects the composition of methanogenic leachate. This is because the high BOD of the acid phase leachate will be consumed as the leachate passes through the well decomposed, and thus carbon limited refuse. Given these caveats, the best approach is to focus on unusual trends or apparent outliers in the leachate data.

With the exception of Landfill M and the NE cell at Landfill Y, acidic pHs were observed at some time in the other landfills, typically in connection with the burial of fresh refuse or initiation of leachate recirculation. For all data sets, the pH ultimately recovered to above 7, suggesting optimal conditions for methanogenesis, given the caveat above on the extent to which leachate chemistry reflects the entire refuse depth. The acidic pHs likely result from an imbalance in the activity of the hydrolytic and fermentative bacteria that produce carboxylic acids, and the microbial population that consumes acetate and generates  $\text{CH}_4$  and  $\text{CO}_2$ . Acidic pHs were not observed at Landfill M or in the NE cell at Landfill Y. At Landfill Y, no pH data were available for the

first year when an acidic pH may have been present. The leachate data from Landfill M reflect refuse that is 5–8 years old, by which time stable methanogenesis would have been established.

The BOD:COD had a tendency to decrease with time as predicted from refuse decomposition theory (Kjeldsen et al. 2002). The relatively high mean BOD:COD for Sump PCS2 and Cell E at Landfill D, and Landfill G likely reflects the influences of fresh refuse and the initiation of recirculation. An increase in BOD:COD reflects an accumulation of carboxylic acids, as discussed above.

There was a tendency for  $\text{NH}_3\text{-N}$  concentrations to increase with time at several of the landfills, as was reported previously (Benson et al. 2007). Ammonia is released by the hydrolysis of proteins that may be present in food and yard waste as well as in biosolids. Thus, ammonia would be expected to accumulate as refuse decomposition proceeds. The highest mean  $\text{NH}_3\text{-N}$  concentration was reported for the control cell at Landfill M, whereas Landfill G exhibited the most pronounced increase in  $\text{NH}_3\text{-N}$  concentration. While speculative, Landfill G accepts septic system waste at the on-site wastewater treatment plant, which probably results in higher concentrations of  $\text{NH}_3\text{-N}$  applied to the landfill. In a review of ammonia toxicity (Parkin and Owen 1986),  $\text{NH}_3\text{-N}$  concentrations of 1,500 mg/L at pH 7 were not toxic and, with acclimation, concentrations that are five times higher were not toxic. Thus, in no case do the  $\text{NH}_3\text{-N}$  concentrations observed for any landfill approach levels considered inhibitory.

### Heavy Metals

Concentrations of heavy metals in leachate from each landfill are summarized in Table 4 along with their maximum contaminant levels (MCLs). As trends with time were not observed for any metal, only means and ranges are presented in Table 4. Leachate metal concentrations are influenced by a number of factors including pH, solubility, moisture content, ion exchange, complex formation, surface adsorption, and colloid content (Christensen et al. 2001; Gould et al. 1990). Thus, environmental conditions, rather than the initial quantity of a metal buried, have the most influence on metals concentrations in leachate.

The attenuation capacity of refuse for metals has been demonstrated in previous work in which industrial sludges with elevated concentrations of Cd, Cr, Ni, Hg, Pb, and Zn were added to refuse columns that were operated with and without leachate recirculation (Gould et al. 1990). Metals concentrations decreased substantially as the refuse transitioned from the acid phase to the methane phase, with a concurrent pH increase. In some cases, addition of sludge only impacted metals concentrations when added at moderate and high levels, whereas in other cases, there was no difference in leachate concentration regardless of the metals dose, supporting the aforementioned suggestion that environmental conditions control leachate metal concentrations.

The only possible comparison of control and bioreactor leachates was at Landfill M, although the bioreactor and control cell refuse are not the same age. The data do not suggest differences between these two cells at Landfill M. There was not a consistent trend in the means between the W and NE cells at Landfill Y nor across cells at Landfill D.

Metals that were detected consistently (>50% of all analyses) include As, Ba, Cr, Cu (at Landfills Y, G, and L), Pb, Se (at Landfills Y and L), and Zn. Cd, Cu (Landfill D), Hg, and Se were detected in less than 50% of analyses. Means were calculated using the samples with detected concentrations only, and thus are

**Table 4.** Concentrations of Metals in Leachate from Landfills in This Study and Literature Ranges ( $\mu\text{g/L}$ )

Landfill M										
Metal	MCL	Control			Bioreactor			Leachate tank		
		Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range
As	10	96	62	30–140	57	20	10–30	79	34.5	30–40
Ba	2,000	100	528.4	106–1,050	100	811	110–1,100	100	438	181–810
Cd	5	8	1.5	0.9–2.1	0	—	—	7	0.9	—
Cr	100	100	264.5 <sup>b</sup>	10–1,980	96	54.6	20–350	100	132	110–170
Cu	1,300	nm	nm	nm	nm	nm	nm	nm	nm	nm
Ph	15	4	6	—	0	—	—	0	—	—
Hg	2	0	—	—	0	—	—	0	—	—
Se	50	35	7.6	5–13	0	—	—	29	5.5	5–6
Zn <sup>a</sup>	5,000	nm	nm	nm	nm	nm	nm	nm	nm	nm

Landfill D													
Metal	MCL	Cell C			Cell D PCS-1			Cell D-PCS2			Cell E		
		Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range
As	10	90.3	20	10–130	93.3	20	10–40	96.2	20	6–33	66.7	20	10–50
Ba	2,000	100	420	200–1,100	100	550	230–3,200	100	450	233–940	100	730	320–2,700
Cd	5	5.1	10	1–20	16.7	10	1–17	19.2	10	2–180	46.7	2	1–8
Cr	100	93.5	30	10–100	93.3	40	16–70	100	50	6–140	53.3	40	10–120
Cu	1,300	12.9	20	10–40	0	—	—	3.8	40	—	0	—	—
Ph	15	19.4	10	6–70	23.3	70	8–190	50	30	7–90	46.7	20	10–80
Hg	2	3.3	1.3	0.6–2	0	—	—	0	—	—	0	—	—
Se	50	11.9	60	10–109	11.5	10	10–20	13.6	20	10–30	13.3	10	—
Zn <sup>a</sup>	5,000	71.5	1,350	8–112,000	95.5	400	20–6,400	95.4	1,600	20–47,600	94.4	840	20–6,890

Landfill L													
Metal	MCL	Landfill G			Area C Cell 1			Area C Cell 2			Tank		
		Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range
As	10	75.4	84.8	6–155	97.2	30.7	6–144	97.1	36.9	5–126	100	63.6	9–311
Ba	2,000	nm	nm	nm	100	289	99–585	100	302	75–653	100	280	118–974
Cd	5	nm	nm	nm	2.8	5	—	2.9	7	—	7.9	4.7	4–5
Cr	100	93.4	102	15–419	100	83.7	11–235	94.3	115	8–293	100	53.8	10–126
Cu	1,300	63.9	55.8	4–210	88.9	31	4–185	100	84.4	7–490	81.6	17.9	3–101
Ph	15	55.7	55.6	3–300	50	9.5	2–40	51.4	8.5	2–15	21	4.6	2–14
Hg	2	nm	nm	nm	13.9	2.5	0.3–8.7	5.7	0.5	0.3–0.7	18.4	0.6	0.2–1.1
Se	50	nm	nm	nm	66.7	9.6	3–24	71.4	10.1	2–57	60.5	6.6	2–21
Zn <sup>a</sup>	5,000	100	1,569	45–10,600	97.2	79	13–218	94.3	150	13–1,040	94.7	62.8	13–376

Landfill Y											
Metal	MCL	NE			W			Kjeldsen et al. (2002)		Outer Loop <sup>c</sup>	
		Detect (%)	Mean	Range	Detect (%)	Mean	Range	Range	Detect (%)	Mean	Range
As	10	100	64.7	23–120	100	67.6	2.8–270	10–1,000	100	120	10–270
Ba	2,000	100	1,230	390–2,500	100	2,010	450–4,300	nr	100	790	330–940
Cd	5	26.1	0.28	0–2.9	36.4	0.45	0–2.4	0.1–400	3	1	1
Cr	100	95.6	76	0–170	90.1	49.2	0–160	20–1,500	100	70	30–10
Cu	1,300	91.3	7.6	0–30	95.4	5	0–13	5–10,000	27	20	10–20
Ph	15	87	1.7	0–5	68.2	1.5	0–8.4	1–5,000	41	10	10–20
Hg	2	21.7	0.02	0–0.16	22.7	0.03	0–0.23	0.05–160	nr	—	—
Se	50	56.5	18.8	0–70	59.1	16.3	0–55	nr	nr	—	—
Zn <sup>a</sup>	5,000	73.9	103	0–1,000	81.8	162	0–2,400	30–10 <sup>6</sup>	69	75	30–170

Note: All data are in  $\mu\text{g/L}$ ; —=0 or 1 detects; nm=not measured; nr=not reported. Means do not include samples in which the metal was not detected.

<sup>a</sup>For Zn, a secondary drinking water standard (<http://www.epa.gov/safewater/contaminants/index.html>).

<sup>b</sup>Includes one outlier of 1,980 mg/L; if excluded, then the mean is 196 mg/L.

<sup>c</sup>Data are the average of two data sets associated with replicate sections of a retrofit bioreactor (U.S. EPA 2006).



biased upward. The ranges and detection frequencies summarized in Table 4 are consistent with data from bioreactor cells at the Outer Loop Landfill in Louisville, Kentucky (U.S. EPA 2006) and were within the ranges reported by Kjeldsen et al. (2002) (Table 4). Given the age of the data in Kjeldsen et al. (2002), the data almost certainly do not include bioreactor landfills. Thus, this comparison suggests that metals concentrations in bioreactor leachates are no different from conventional leachates. Zn was present in the highest concentrations in the data from this study and in previous studies (Gould et al. 1990; Kjeldsen et al. 2002). Metals concentrations typically were below their MCL, although the MCL is an unrealistically stringent benchmark as leachate is treated and diluted at modern landfills before it is released to the environment.

The only metal that was consistently above the MCL was As. The ranges for As from this study are consistent with ranges in the literature (Baun and Christensen 2004). Sources of As in landfills include glass, soil, metal alloys, and agricultural products (Pinel-Raffaitin et al. 2007). Although sufficient data are not available to indicate whether As concentrations have increased in landfill leachate with time, the mass of As entering landfills is anticipated to increase as more As is removed from drinking water and the treatment residuals are disposed in landfills. Recently, Ponthieu et al. (2007) reported speciated As concentrations in leachate from several French landfills cells that received primarily MSW. Total As ranged from 17 to 77  $\mu\text{g/L}$  which is similar to the range in Table 4. Comparing leachate As in traditional and bioreactor leachate, more of the As in the bioreactor leachate was in the nontoxic arsenobetaine form. The writers suggested that enhanced biological activity in the bioreactor may have converted more toxic forms of organic As to arsenobetaine.

In summary, there is no evidence that bioreactor landfill leachate contains higher metals concentrations than conventional landfills. Rather, the neutral pH associated with the onset of methane production is likely the critical factor controlling metals concentrations. As bioreactor landfills are operated to enhance methanogenic conditions, bioreactor landfill leachate will have less time in the acid phase when metals concentrations will be highest.

### **Speciated Organic Chemicals**

Speciated organic chemical concentrations in leachate from each landfill are summarized in Table 5. Only data for compounds that were detected in greater than 50% of samples at any one landfill are presented. Means were calculated based only on detected samples and thus represent an upper limit. Leachate concentrations are influenced by a number of factors including sorption, volatilization, biodegradation, refuse moisture content, the initial mass input (which is unknown), and dilution from infiltration. Thus, mechanistic interpretation of the reported data are difficult.

At Landfill D, the following chemicals exhibited a decreasing trend with time: acetone, m/p-cresol, ethyl ether, ethylbenzene, 2-butanone, 4-methyl-2-pentanone, methylene chloride, naphthalene, phenol, total phenolics, and toluene; whereas no trends were apparent for tetrahydrofuran (THF), m/p-xylene, and o-xylene. Toluene concentrations at Landfill D are presented in Fig. 10 as an example of a decreasing trend. With the exception of decreasing toluene concentrations at Landfill L, no other trends were apparent at any landfill.

The lower toluene concentrations in Cell E at Landfill D between Years 1 and 3 (Fig. 10) roughly correspond to a period of high rainfall. As Cell E was active during this period, higher

infiltration would be expected relative to the other cells. However, counteracting dilution, high rainfall would also increase the degree of saturation in the cover soils, thereby decreasing diffusive losses. Also in Cell E, the concentrations of acetone, m/p cresol, ethyl ether, MEK (2-butanone), 4-methyl-2-pentanone, THF, and toluene increased starting around Year 6 (data not shown). This increase corresponds approximately to the onset of leachate recirculation in Cell E. These contaminants have high water solubilities (exception toluene), and they may have dissolved into leachate as it percolated through the landfill.

Separate concentration data were available for the bioreactor and control cells and the leachate tank at Landfill M. Where the same compound was detected in both the bioreactor and control cells, there was no trend in mean concentrations between the two. Because there was no overlap of waste ages between the two cells, a direct comparison of the leachate concentrations is imperfect. The mean vinyl chloride concentration exceeded the MCL in several samples in the bioreactor cell, but was never detected in the leachate tank. The mean benzene concentration was above the MCL in the bioreactor leachate and close to the MCL in the control and tank leachate. While benzene was detected at greater frequency in the bioreactor cell, other aromatics were detected at greater frequency in the control cell. Thus, the data do not support increased dissolution in the wetter bioreactor. In no case did the concentrations of a contaminant in the leachate tank exceed the MCL.

In general the same compounds were detected at comparable frequencies in the NE and W cells at Landfill Y. As for Landfill M, benzene and vinyl chloride were detected above their MCL in selected samples. Other compounds present above their MCL included dichloromethane and tetrachloroethene, at maximum concentrations of 10 and 6.2  $\mu\text{g/L}$ , respectively. However, detection frequencies for these chemicals were less than 10%.

Benzene and vinyl chloride were present at mean concentrations above their MCLs in leachate from Landfills G and L, as well as in the leachate tank at Landfill L. This tank receives leachate from the entire landfill as opposed to the bioreactor area only. Contaminants in Landfill L leachate were generally detected at similar frequencies from the two leachate sample locations and the leachate tank.

Ranges of trace organics concentrations measured in landfill leachate at other landfills are also summarized in Table 5. As for metals, the literature data almost certainly do not include bioreactor landfills. In no case are the concentrations for any of the landfills evaluated in this study above the literature values.

Alkylbenzenes, phenolic compounds, and ketones were most consistently detected across the five study landfills. THF and ethyl ether, which were only analyzed at Landfill D, and methyl tert-butyl ether (MTBE), which was only analyzed at Landfill Y, were also detected frequently. Alkylbenzenes and ketones are present in a wide variety of household products so their presence in leachate is expected. Aromatic hydrocarbons are routinely present in LFG (Allen et al. 1997; Eklund et al. 1998). In addition, ketones can be produced under anaerobic conditions (Woods 1995). In previous research, acetone and 2-butanone were released during anaerobic decomposition, suggesting their continuous production (Staley et al. 2006). This would explain the relatively high concentrations reported here and the consistency across landfills.

The concentration of volatile organic chemicals (VOCs) can be expected to decrease with time based on gas stripping, an effect that has been quantified using an equilibrium model (Kjeldsen and Christensen 2001). In some cases, biodegradation probably contributed to the decreases in VOC concentrations.

**Table 5.** Concentrations of Selected Organic Compounds in This Study and Literature Ranges ( $\mu\text{g/L}$ )

Organic compound	MCL	Landfill M									Landfill Y					
		Bioreactor cell			Control cell			Tank			NE			West		
		Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range
Benzene	5	57	7.59	5.6–10	14	4.88	3.3–6.6	7	4.6	4.6	26	2.0	0.4–3.2	41	5.10	2.9–75
Toluene	1,000	21	10.4	2.3–17	86	127	34–326	79	78.8	16.9–380	61	12.10	1.9–24	82	19.3	2.2–56
Ethylbenzene	700	82	46.7	5.6–134	75	30.3	11.8–58	21	11.9	7–19.8	39	2.60	0.6–5.3	45	4.00	2.3–5.5
Total xylenes	10,000	100	122	6–336	89	92.1	35.5–194	71	30.4	7.1–62	39	6.20	1.5–15	36	12.70	3.6–44.1
Phenol		11	745.0	11–2,200	79	3,148	580–9,660	64	706	12–3,600	nm	nm	nm	nm	nm	nm
m/p cresol (3/4 methylphenol)		7	16.0	16.0	57	1,250	29–4,300	57	84.3	34–134	nm	nm	nm	nm	nm	nm
Acetone		29	1,530.0	10–12,100	71	7,560	13.6–46,600	57	9,254	26.1–23,600	70	204	6.4–2,300	41	5.1	2.9–75
MEK (2-butanone)		21	25.0	5–52.1	71	9,913	6–62,900	71	10,104	10.4–30,500	26	1,358	2–4,300	9	39.1	3.3–75
Methyl butyl ketone (2-hexanone)		0	—	—	29	32.0	12.2–14.2	0	—	—	4	26.00	26	0	—	—
4-methyl-2-pentanone		21	270.0	5–800	50	523	3.4–1,460	57	295	55–646	48	198	2–1,000	32	198.8	2.1–1,200
1,1-dichloroethane		14	3.90	1.8–6.0	0	—	—	0	—	—	22	1.8	0.8–2.5	27	6.6	1.0–13.0
1,4-dichlorobenzene	75	89	14.2	9.3–26.0	54	11.5	6.5–16		—	—	0			nd	nd	nd
Chloroethane		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
cis-1,2-dichloroethylene	70	nm	nm	nm	nm	nm	nm	nm	nm	nm	30	2.2	0.8–5.2	5	1.3	1.3
Dichloromethane	5	nm	nm	nm	nm	nm	nm	nm	nm	nm	13	3.90	0.23–10	5	5.80	5.8
Vinyl chloride	2	18	5.80	3.0–14.0	4	2.00	2.00	0	—	—	22	3.50	0.4–6.7	27	5.3	2.8–10
Naphthalene		32	14.9	10.0–22.0	21	21.5	10.0–38.0		—	—	0	—	—	5	2.8	2.8
Tetrahydrofuran		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Ethyl ether		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Acetonitrile		25	199	21.5–1,060	82	513	78–1,450	64	204	123–417	nm	nm	nm	nm	nm	nm
1,1-dichloroethene		0	—	—	0	—	—	0	—	—	0	—	—	nd	—	—
Tetrachloroethene	5	0	—	—	0	—	—	0	—	—	0	—	—	5	6.2	—
Trichloroethene	5	0	—	—	0	—	—	0	—	—	0	—	—	0	—	—
MTBE		nm	nm	nm	nm	nm	nm	nm	nm	nm	86	26.8	6.3–110	86	119	37–210

Organic compound	MCL	Landfill D														
		Area C			Area D PCS #1			Area D PCS #2			Area E			Leachate tank		
		Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range
Benzene	5	22	5.2	2–11	15	8.75	8–11	36	5.9	3–9	67	9.9	6.2–13	0	—	—
Toluene	1,000	81	209	5–718	92	203.2	10.7–606	95	170.1	22–450	100	165.7	87.3–270	93	26.5	5.3–48

Table 5. (Continued.)

		Landfill D															
		Area C			Area D PCS #1			Area D PCS #2			Area E			Leachate tank			
Organic compound	MCL	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	
Ethylbenzene	700	72	138.9	9.3–606	85	70.8	6–131	86	28	9–64.5	100	36.4	9.2–65.7	73	16.4	6.1–72.6	
Total xylenes	10,000	64	121.7	16.6–460	85	116	36–184	91	74.9	33–150	100	80.1	29–136	60	34.9	18–64	
Phenol		50	585	13–2,490	31	882.6	280–1,800	41	406.1	52–1,100	73	153.6	51–407	13	278.5	54–503	
m/p cresol (3/4 methylphenol)		36	857.4	42–6,300	38	2,870	169–7,200	73	1,157	122–4,500	93	1,501	372–5,490	40	631.8	124–2,630	
Acetone		64	1,224	75–5,900	54	3,290	110–9,800	82	1,137	83–4,500	100	1,986	36–7,490	53	628.7	21–4,210	
MEK (2-butanone)		64	2,311	33–18,000	58	5,794	70.4–15,000	91	2,132	110–12,000	100	4,185	251–20,700	47	1,707	30–10,400	
Methyl butyl ketone (2-hexanone)		0	—	—	15	88.3	47–190	18	38	6–68	13	74.8	51–98.6	7	48	—	
4-methyl-2-pentanone		28	556.5	31–4,600	19	240	180–330	73	81.2	18–290	87	86.4	21–265	13	26.1	9.2–43	
1,1-dichloroethane		28	69.1	1–270	15	35.8	7–91	50	32.5	14–58	47	250.9	2.9–1,710	0	—	—	
1,4-dichlorobenzene	75	19	12.1	6–18	0	—	—	9	5.5	4–7	0	—	—	0	—	—	
Chloroethane		6	20	10–30	12	28.7	14–47	50	16.2	7.6–32	0	—	—	0	—	—	
cis-1,2-dichloroethylene	70	11	11.3	3–20	8	7.5	5–10	23	12	11–13	67	13.5	6.4–25	0	—	—	
Dichloromethane	5	33	361.6	4–820	35	564.2	20–2,710	59	162.2	16–600	73	53.6	5.6–270	7	14	—	
Vinyl chloride	2	0	—	—	4	12	—	0	—	—	40	9.1	5.2–18	0	—	—	
Naphthalene		42	160.5	15–620	23	40.5	14–166	9	36	19–53	13	16.5	15–18	0	—	—	
Tetrahydrofuran		61	1,118	279–11,000	77	1,783	1,000–2,820	91	1,451	250–2,850	93	1,281	144–3,680	93	591.6	366–1,060	
Ethyl ether		36	18.4	7.6–43	65	95.1	11–300	77	169.9	33–700	100	136.4	50–261	100	27	10–51	
Acetonitrile		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	
1,1-Dichloroethene		nd	—	—	nd	—	—	nd	—	—	nd	—	—	nd	—	—	
Tetrachloroethene	5	nd	—	—	nd	—	—	nd	—	—	nd	—	—	nd	—	—	
Trichloroethene	5	nd	—	—	nd	—	—	nd	—	—	nd	—	—	nd	—	—	
MTBE		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	
Landfill L															Christensen et al. (2001)		
		Landfill G			Area C Cell 1			Area C Cell 2			Tank			Outer loop landfill, Kentucky			
Organic compound	MCL	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Range	Detect (%)	Mean	Range
Benzene	5	41	25	2–250	56	8.5	4.5–16	66	7.6	5–10	42	10.9	5.2–36.3	1–1,630	19	9.9	7.1–12

Table 5. (Continued.)

Organic compound	MCL	Landfill L												Christ- ensen et al. (2001)	Outer loop landfill, Kentucky		
		Landfill G			Area C Cell 1			Area C Cell 2			Tank						
		Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Detect (%)	Mean	Range	Range	Detect (%)	Mean	Range
Toluene	1,000	85	223	6–734	92	255.7	9.3–1,250	94	252.4	6.5–700	97	240.7	7–1,270	1– 12,300	100	96.4	20– 200
Ethylbenzene	700	75	27	6–73	81	47.8	7.1–197	89	42.4	11–117	95	81.0	7.9–533	1– 1,280	100	49.9	28– 100
Total xylenes	10,000	90	85	4–488	100	140.2	9.9–680	94	157.5	38–387	100	338.9	18–2,084	4– 3,500	100	123	68– 280
Phenol		nm	nm	nm	75	900	50–3,200	80	500	50–3,090	66	2,600	100– 25,000	1– 1,200	45	233	73– 670
phenolics for L		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	1– 2,100	86 (p- cresol)	824	33– 4,400
m/p cresol (3/4 methylphenol)																	
Acetone		57	2,973	55–29,100	92	3,952.9	24–31,500	100	2,238.1	11–19,500	100	5,040.1	482– 17,350	6– 4,400	75	82.2	73– 2,000
MEK (2-butanone)		69	6,198	16–51,000	89	7,895.9	35–59,500	91	4,194.0	10–28,500	100	6,427.9	422– 25,600	nr	67	2,399	70– 10,000
Methyl butyl ketone (2-Hexanone)		23	170	1–443	36	31.2	10–74	40	19.4	10–35	34	67.9	11–413	nr	nr		
4-methyl-2-pentanone		57	189	16–992	72	183.1	11–900	69	102.4	12–238	97	302.8	15–3,600	nr	nr		
1,1-dichloroethane		nm	nm	nm	44	35.6	5.6–104	54	42.3	5–100	24	16.3	5.9–34.0	nr	nr		
1,4-dichlorobenzene	75	nm	nm	nm	69	14.7	5.7–78	91	12.8	6.1–32	97	70.3	5.9–528	0.1– 16	7	17.8	14– 24
chloroethane		nm	nm	nm	19	17.7	10–28	31	18.3	6.1–32	3	5.6		nr	nr		
cis-1,2- dichloroethylene	70	nm	nm	nm	31	20.6	5.4–60	37	25.5	7.8–44	42	18.2	5.1–86	nr	nr		
Dichloromethane	5	nm	nm	nm	31	484.4	5.9–2,300	46	399.5	6.2–2,090	37	234.2	6.6–1,600	1–64	nr		
Vinyl chloride	2	13	67	1.5–500	53	14.0	2.2–64	60	11.3	2–59	39	5.6	2–14	nr	nr		
Naphthalene		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	0.1– 260	nr		
Tetrahydrofuran		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nr	nr		
Ethyl ether		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nr	nr		
Acetonitrile		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nr	nr		
1,1-dichloroethene		25	91	3.7–235	3	5	—	6	56.5	20–93	0	—	—	nr	nr		
Tetrachloroethene	5	20	45	1–250	17	65.5	8–133	26	55	11–134	16	23.9	5.3–63	0.1– 250	nr		
Trichloroethene	5	25	40	1.9–250	19	19.2	7.2–23	29	15.9	5.7–30	21	15.4	7.4–36.8	0.7– 750	nr		
MTBE		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nr	nr		

Note: —=0 or 1 detects; nm=not measured; nd=not detected; nr=not reported.

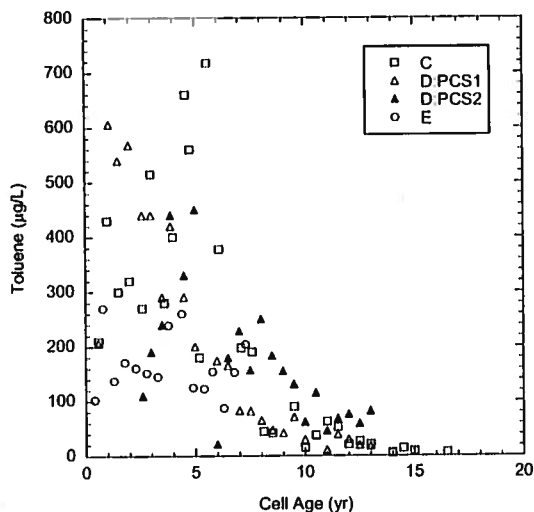


Fig. 10. Toluene concentration in Landfill D leachate

Biodegradation under simulated landfill conditions has been demonstrated for a few compounds (acetone, toluene, phthalic acid esters, phenol, o-cresol, and selected chlorinated aliphatics) as reviewed in Hilger and Barlaz (2006). In contrast, methanogenic biodegradation of naphthalene has only recently been reported and is not thought to be widespread (Chang et al. 2006). Thus, the decrease in naphthalene concentration at Landfill D probably is not due to biodegradation.

In summary, decreasing trends were observed for several organic chemicals. Biodegradation probably contributed to these trends, but evidence to confirm the role of biodegradation is not available. Benzene and vinyl chloride were most commonly detected above MCLs. Both of these chemicals are sufficiently volatile that the leachate concentration is likely influenced by the sampling point. For example, leachate stored in a tank is likely to release VOCs prior to sampling.

## Summary and Conclusions

In all cases, leachate from a wider landfill footprint was used to supply leachate to the landfill section operated as a bioreactor. Thus, the bioreactor refuse mass was handling leachate generated from a larger mass. The data support accelerated methane generation at several landfills relative to rates predicted using AP-42 default values, which has several implications. First, it is important to initiate gas collection quickly once moisture addition begins to minimize methane emissions. Second, the higher rates of gas production in bioreactor landfills must be considered in the size and design of gas collection systems, and also in economic evaluations of LFG to energy projects. Third, gas generation can be expected to decrease more rapidly after refuse burial ceases. Thus, the scope and duration of gas collection and monitoring may be decreased more rapidly at bioreactor landfills after landfill closure.

The data collected in this study indicate that gas production increases as the amount of moisture added to the waste increases. A relationship between decay rate and total moisture added to the waste was identified for bioreactor landfills that incorporated horizontal recirculation trenches during filling. However, a general relationship between decay rate and moisture added or water

content could not be identified. There was no indication that gas production increases appreciably when the water content of a bioreactor landfill reaches 40%.

Most of the leachates at the landfills in this study were commingled from various cells. In addition, most of the leachate contacted waste of different ages. While these factors confound an evaluation of the impact of bioreactor operations on leachate composition, the observations here represent the state-of-the-practice. Nevertheless, trends in pH and BOD:COD in the bioreactor leachates were consistent with the impacts of enhanced biological activity. Ammonia concentrations at the bioreactor landfills also increased over time, as was observed in a previous study (Benson et al. 2007). In the context of contaminants of concern (e.g., heavy metals, speciated organic chemicals), there is no indication that bioreactor landfill leachate is significantly different from leachate generated at conventional landfills. For most contaminants of concern, concentrations in leachate were below MCLs (exceptions include As and several organic compounds). Concentrations of many of the volatile organic compounds decreased over time, most likely due to gas stripping and biodegradation.

The in situ treatment of leachate by recirculation decreases energy consumption at aerobic wastewater treatment facilities. In addition, some landfills must transport leachate off-site for treatment, e.g., Sites M and D in this study. The avoidance of off-site transport results in decreased truck transport and associated air emissions. Furthermore, there is increasing capacity pressure at many publicly owned wastewater treatment plants and some have notified landfill owners that leachate may not be accepted in the future. The in situ treatment of some leachate can help to mitigate capacity problems.

This study documents several of the purported advantages of bioreactor landfills. With these advantages come increased operational requirements to manage leachate and gas.

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## References

- Allen, M. R., Braithwaite, A., and Hills, C. C. (1997). "Trace organic compounds in landfill gas at seven UK waste disposal sites." *Environ. Sci. Technol.*, 31, 1054–1061.
- Bareither, C. A., Benson, C. H., Barlaz, M. A., Edil, T. B., and Tolaymat, T. M. (2010). "Performance of North American bioreactor landfills. I: Leachate hydrology and waste settlement." *J. Environ. Eng.*, 136(8), 824–838.
- Baun, D. L., and Christensen, T. H. (2004). "Speciation of heavy metals in landfill leachate: A review." *Waste Manage. Res.*, 22(1), 3–23.
- Benson, C. H., Barlaz, M. A., Lane, D. T., and Rawe, J. M. (2007). "Practice review of five bioreactor/recirculation landfills." *Waste*



- Manage.*, 27(1), 13–29.
- Chang, W., Um, Y., and Holoman, T. R. P. (2006). "Polycyclic aromatic hydrocarbon (PAH) degradation coupled to methanogenesis." *Bio-technol. Lett.*, 28(6), 425–430.
- Christensen, T. H., et al. (2001). "Biogeochemistry of landfill leachate plumes." *Appl. Geochem.*, 16(7–8), 659–718.
- Eklund, B., Anderson, E. P., Walker, B. L., and Burrows, D. B. (1998). "Characterization of landfill gas composition at the fresh kills municipal solid-waste landfill." *Environ. Sci. Technol.*, 32, 2233–2237.
- Faour, A., Reinhart, D. R., and You, H. (2007). "First-order kinetic gas generation model parameters for wet landfills." *Waste Manage.*, 27(7), 946–953.
- Gould, J. P., Cross, W. H., and Pohland, F. G. (1990). "Factors influencing mobility of toxic metals in landfills operated with leachate recycle." *Amer. Chem. Soc. Symp. Series*, 422, 267–291.
- Haydar, M. M., and Khire, M. V. (2005). "Recirculation using horizontal trenches in bioreactor landfills." *J. Geotech. Geoenviron. Eng.*, 131(7), 837–847.
- Hilger, H. H., and Barlaz, M. A. (2006). "Anaerobic decomposition of refuse in landfills and methane oxidation in landfill cover soils." *Manual of environmental microbiology*, 3rd Ed., Am. Soc. Microbiol., Washington, D.C.
- Hull, M. R., Krogmann, U., and Strom, P. F. (2005). "Composition and characteristics of excavated materials from a New Jersey landfill." *J. Environ. Eng.*, 131(3), 478–490.
- Kjeldsen, P., Barlaz, M. A., Rooker, A. P., Baun, A., Ledin, A., and Christensen, T. H. (2002). "Present and long term composition of MSW landfill leachate—A review." *Crit. Rev. Environ. Sci. Technol.*, 32(4), 297–336.
- Kjeldsen, P., and Christensen, T. H. (2001). "A simple model for the distribution and fate of organic chemicals in a landfill: MOCLA." *Waste Manage. Res.*, 19, 201–216.
- Morris, J. W. F., Vasuki, N. C., Baker, J. A., and Pendleton, C. H. (2003). "Findings from long-term monitoring studies at MSW landfill facilities with leachate recirculation." *Waste Manage.*, 23, 653–666.
- Parkin, G. G., and Owen, W. F. (1986). "Fundamentals of anaerobic digestion of waste sludges." *J. Environ. Eng.*, 112(5), 867–921.
- Pinel-Raffaitin, P., Le Hecho, I., Amouroux, D., and PotinGautier, M. (2007). "Distribution and fate of inorganic and organic arsenic species in landfill leachates and biogases." *Environ. Sci. Technol.*, 41(13), 4536–4541.
- Ponthieu, M., et al. (2007). "Speciation analysis of arsenic in landfill leachate." *Water Res.*, 41(14), 3177–3185.
- Staley, B. F., and Barlaz, M. A. (2009). "Composition of municipal solid waste in the U.S. and implications for carbon sequestration and methane yield." *J. Environ. Eng.*, 135(10), 901–909.
- Staley, B. F., Xu, F., Cowie, S. J., Barlaz, M. A., and Hater, G. R. (2006). "Release of trace organic compounds during the decomposition of municipal solid waste compounds." *Environ. Sci. Technol.*, 40(19), 5984–5991.
- Tolaymat, T. M., et al. (2010). "Evaluation of landfill gas decay constant for municipal solid waste landfills operated as bioreactors." *J. Air Waste Manage. Assoc.*, 60, 91–97.
- U.S. EPA. (1998). "AP-42 emission factors for municipal solid waste landfills—Supplement E, November 1998." (<http://www.epa.gov/ttn/chief/ap42/ch02/final/c02s04.pdf>) (February 2007).
- U.S. EPA. (2003). "National emission standards for hazardous air pollutants: Municipal solid waste landfills." *40 CFR Part 63*, Washington, D.C., 2227.
- U.S. EPA. (2005). "Landfill gas emissions model (LandGEM) version 3.02 user's guide." *Rep. No. EPA/600/R-05/047*, Research Triangle Park, N.C.
- U.S. EPA. (2006). "Landfill bioreactor performance: Second interim report—outer loop recycling & disposal facility, Louisville, Kentucky." *Rep. No. EPA/600/R-07/060*, Cincinnati.
- Woods, D. R. (1995). "Genetic-engineering of microbial solvent production." *Trends Biotechnol.*, 13, 259–264.
- Yazdani, R., Kieffer, J., Sananikone, K., and Augenstein, D. (2006). "Full scale bioreactor landfill for carbon sequestration and greenhouse emission control." *Final Technical Progress Rep., DOE Award # DE-FC26-01NT41152*, (<http://www.yolocounty.org/Index.aspx?page=438>) (February 2007).